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Direct/Delayed Response Project: Quality Assurance Report for Physical and Chemical Analyses of Soils from the Mid-Appalachian Region of the United States

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Direct/Delayed Response Project: Quality Assurance Report for Physical and Chemical Analyses of Soils from the Mid-Appalachian Region of the United States

by

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A Contribution to the
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The Direct/Delayed Response Project was designed to address the concern over potential acidification of surface waters by atmospheric sulfur deposition in the United States. The purpose of these synoptic soil physical and chemical surveys was to characterize watersheds in regions of the United States believed to be susceptible to the effects of acidic deposition. This document describes the implementation of a quality assurance program and the verification of the analytical data base for the Mid-Appalachian Soil Survey. It is directed primarily towards the users of the data base who will be analyzing the data and making various assessments and conclusions relating to the effects of acidic deposition on watersheds of the region.

The results show that the measurement quality objectives for detectability, precision, accuracy, representativeness, and completeness were generally satisfied. Measurement uncertainty was generally low in relation to overall data uncertainty. A series of conclusions and recommendations are provided at the end of the report. The recommendations will be useful in the planning of future projects of this nature.

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This document is one volume of a set which fully describes the Direct/Delayed Response Project, Mid-Appalachian Soil Survey. The complete document set includes the major data report, quality assurance plan, laboratory analysis handbook, field and preparation laboratory operations and quality assurance reports, and analytical laboratory quality assurance reports. Similar sets are being produced for each Aquatic Effects Research Program component project. Colored covers, artwork, and the use of the project name in the document title serve to identify each companion document set.

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Abstract

The Direct/Delayed Response Project was designed to address the concern over potential acidification of surface waters by atmospheric sulfur deposition in the United States. The Mid-Appalachian Soil Survey was the last of three DDRP surveys conducted from 1985 through 1989. The purpose of these synoptic soil physical and chemical surveys was to characterize watersheds in regions of the United States believed to be susceptible to the effects of acidic deposition. This document describes the implementation of a quality assurance program and the verification of the analytical data base for the Mid-Appalachian Soil Survey. It is directed primarily towards the users of the data base who will be analyzing the data and making various assessments and conclusions relating to the effects of acidic deposition on watersheds of the region.

The quality assurance program was designed in order to satisfy predefined measurement quality objectives and to assess the measurement uncertainty of field sampling, sample preparation, and laboratory analysis. The objectives were directed towards the attributes of detectability, precision, accuracy, representativeness, completeness, and comparability. The quality assurance program uses quality evaluation and quality control samples and is described and evaluated for its ability to identify and resolve potential deficiencies during the survey that would otherwise have had an adverse effect on the data quality. The computerized analytical data entry system "LEVIS" is also evaluated. Summary estimates of measurement uncertainty in relation to overall data uncertainty are provided.

The fifty analytical laboratory parameters included in the analytical data base are segregated into nine groups to allow comparison among similar parameters. Detectability is assessed in terms of detection limits for instrumentation, contract requirements, and the total system. The assessment of precision relied strongly on the analysis of measurement quality samples as a function of intralaboratory within-batch objectives. Two-tiered precision objectives were established for most of the parameters. A step function statistical method was used to estimate the components and magnitude of measurement uncertainty. Overall variability from measurement and population sources was estimated from routine data. Accuracy was investigated in terms of analytical bias, laboratory differences, and laboratory trends in relation to known reference values. Completeness objectives were defined for all measurement phases. Comparability was approached as a complex issue encompassing three levels of detail. Four types of uncertainty estimates, called delta values, were calculated for each parameter.

The results show that the measurement quality objectives for detectability, precision, accuracy, representativeness, and completeness were generally satisfied. Measurement uncertainty was generally low in relation to overall data uncertainty. A series of conclusions and recommendations are provided at the end of the report. The recommendations will be useful in the planning of future projects of this nature.

This report is submitted in partial fulfillment of Contract Number 68-03-3249 by Lockheed Engineering & Sciences Company, Las Vegas, Nevada, under sponsorship of the U.S. Environmental Protection Agency. The report covers survey activities that occurred from September, 1988, to July, 1989.

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Acronyms and Abbreviations

AAS	atomic absorption spectrometry
AC_BACL	exchangeable acidity in barium chloride triethanolamine
AC_KCL	exchangeable acidity in potassium chloride
AD	analytical duplicate sample
AERP	Aquatic Effects Research Program
AL_AO	extractable aluminum in acid oxalate
AL_CD	extractable aluminum in citrate dithionite
AL_CL	exchangeable aluminum in ammonium chloride
AL_CL2	extractable aluminum in calcium chloride
AL_KCL	exchangeable aluminum in potassium chloride
AL_PYP	extractable aluminum in sodium pyrophosphate
ALSOW	analytical laboratory statement of work
ANC	acid neutralizing capacity
ANOVA	analysis of variance
CA_CL	exchangeable calcium in ammonium chloride
CA_CL2	extractable calcium in calcium chloride
CA_OAC	exchangeable calcium in ammonium acetate
CEC	cation exchange capacity
CEC_CL	cation exchange capacity by ammonium chloride
CEC_OAC	cation exchange capacity by ammonium acetate
CLAY	total clay fraction
C:N	carbon:nitrogen
COS	coarse sand fraction
COSI	coarse silt fraction
CRDL	contract-required detection limit
C:S	carbon:sulfur
C_TOT	total carbon
DDRP	Direct/Delayed Response Project
df	degrees of freedom
DL-QCCS	detection limit quality control check sample
DQO	data quality objective
EGME	ethylene glycol monoethyl ether
EMSL-LV	Environmental Monitoring Systems Laboratory at Las Vegas, Nevada
EPA	U.S. Environmental Protection Agency
ERL-C	Environmental Research Laboratory at Corvallis, Oregon
FAL	low-range field audit sample
FAO	organic field audit sample
FAP	mineral field audit sample
FD	field duplicate sample
FE_AO	extractable iron in acid oxalate
FE_CD	extractable iron in citrate dithionite
FE_CL2	extractable iron in calcium chloride
FE_PYP	extractable iron in pyrophosphate
FIA	flow injection analysis

(continued)

Acronyms and Abbreviations *(continued)*

FES	flame emission spectrometry
FSI	fine silt fraction
FS	fine sand fraction
ICP	*inductively coupled argon plasma*
IDL	*instrument detection limit*
IIDL	*independent instrument detection limit*
IFB	*invitation for bid*
K_CL	*exchangeable potassium in ammonium chloride*
K_CL2	*extractable potassium in calcium chloride*
K_OAC	*exchangeable potassium in ammonium acetate*
LAL	*low-range laboratory audit sample*
LAO	*organic laboratory audit sample*
LAP	*mineral laboratory audit sample*
LEVIS	*Laboratory Entry and Verification Information System*
MASS	*Mid-Appalachian Soil Survey*
MG_CL	*exchangeable magnesium in ammonium chloride*
MG_CL2	*extractable magnesium in calcium chloride*
MG_OAC	*exchangeable magnesium in ammonium acetate*
MOIST	*percent air-dry soil moisture content*
MS	*medium sand fraction*
MQO	*measurement quality objective*
NA_CL	*exchangeable sodium in ammonium chloride*
NA_CL2	*extractable sodium in calcium chloride*
NA_OAC	*exchangeable sodium in ammonium acetate*
NAPAP	*National Acid Precipitation Assessment Program*
NCSS	*National Cooperative Soil Survey*
NE	*Northeastern*
NSWS	*National Surface Water Survey*
N_TOT	*total nitrogen*
ORNL	*Oak Ridge National Laboratory*
P	*percentile*
PD	*preparation duplicate sample*
PE	*performance evaluation*
PH_H2O	*pH in deionized water*
PH_002M	*pH in 0.002M calcium chloride*
PH_01M	*pH in 0.01M calcium chloride*
QA	*quality assurance*
QART	*quality assurance reanalysis template*
QC	*quality control*
QCAS	*quality control audit sample*
QCCS	*quality control check sample*
QE	*quality evaluation*
R	*reference value*
RS	*routine sample*
RSD	*relative standard deviation*
SAND	*total sand fraction*
SBRP	*Southern Blue Ridge Province*
SCR	*soil chemistry relationship*
SCS	*Soil Conservation Service*
SD	*standard deviation*
SDL	*system detection limit*

(continued)

Acronyms and Abbreviations *(continued)*

S/H	sampling class/horizon group
SI_AO	extractable silicon in acid oxalate
SILT	total silt fraction
SO4_0	zero mg S/L sulfate isotherm parameter
SO4_2	two mg S/L sulfate isotherm parameter
SO4_4	four mg S/L sulfate isotherm parameter
SO4_8	eight mg S/L sulfate isotherm parameter
SO4_16	sixteen mg S/L sulfate isotherm parameter
SO4_32	thirty-two mg S/L sulfate isotherm parameter
SO4_H2O	extractable sulfate in deionized water
SO4_PO4	extractable sulfate in sodium phosphate
SP_SUR	specific surface
S_TOT	total sulfur
USDA	U.S. Department of Agriculture
VCOS	very coarse sand fraction
VFS	very fine sand fraction

Executive Summary

Introduction

The U.S. Environmental Protection Agency (EPA), as a participant in the National Acid Precipitation Assessment Program, has designed and implemented a research program to predict the long-term response of watersheds and surface waters in the United States to acidic deposition. Based on this research, a sample of watershed systems will be classified according to the time scale in which each system will reach an acidic steady state, assuming current levels of acidic deposition. The Direct/Delayed Response Project (DDRP) was designed as the terrestrial component of the EPA Aquatic Effects Research Program.

The mapping for the DDRP Mid-Appalachian Soil Survey was conducted in portions of Pennsylvania, Virginia, and West Virginia during the spring and summer of 1988 and the sampling took place the during the fall of 1988. These activities initiated the third full-scale regional survey of the DDRP. The physical and chemical properties that were measured in the soil samples are listed below.

Physical and Chemical Parameters Measured in the Direct/Delayed Response Project Mid-Appalachian Soil Survey

Air-dry moisture content
Total sand
Very coarse sand
Coarse sand
Medium sand
Fine sand
Very fine sand
Total silt
Coarse silt
Fine silt
Total clay
pH in deionized water
pH in 0.002M calcium chloride
pH in 0.01M calcium chloride
Ca in 1.0M ammonium chloride
Mg in 1.0M ammonium chloride
K in 1.0M ammonium chloride
Na in 1.0M ammonium chloride
Al in 1.0M ammonium chloride
Ca in 1.0M ammonium acetate
Mg in 1.0M amonium acetate
K in 1.0M ammonium acetate
Na in 1.0M ammonium acetate
CEC in 1.0M ammonium chloride
CEC in 1.0M ammonium acetate
Ex. Acidity by barium chloride-TEA
Ca in 0.002M calcium chloride
Mg in 0.002M calcium chloride
K in 0.002M calcium chloride
Na in 0.002M calcium chloride
Fe in 0.002M calcium chloride
Al in 0.002M calcium chloride
Ext. Fe in pyrophosphate
Ext. Al in pyrophosphate
Ext. Fe in acid oxalate
Ext. Al in acid oxalate
Ext. Si in acid oxalate
Ext. Fe in citrate dithionite
Ext. Al in citrate dithionite
Ext. sulfate in deionized water
Ext. sulfate in sodium phosphate
Sulfate isotherm 0 mg sulfur
Sulfate isotherm 2 mg sulfur
Sulfate isotherm 4 mg sulfur
Sulfate isotherm 8 mg sulfur
Sulfate isotherm 16 mg sulfur
Sulfate isotherm 32 mg sulfur
Total carbon
Total nitrogen
Total sulfur

Quality Assurance Optimization

As a result of conclusions and recommendations from the DDRP Northeastern region and Southern Blue Ridge Province soil surveys, a number of improvements were made in the quality assurance program for the Mid-Appalachian soil survey. A single preparation laboratory was established in Las Vegas, Nevada, in close proximity to the EPA Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV) quality assurance (QA) staff. This allowed the development of, and adherence to, strictly defined sample preparation protocols and the ability to track and control progress at the laboratory on a real-time basis.

Mineral and organic samples were placed in separate batches because of differences in analyte concentrations and in the soil:solution ratios required for analysis. As a result, the analytical laboratories were able to perform instrument calibration and sample analyses within narrower linear dynamic ranges, allowing the QA staff to make more reliable assessments of the resulting data quality.

Several changes in analytical methods and procedures were initiated in the Mid-Appalachian survey. For example, the exchangeable aluminum in 1M potassium chloride parameter was replaced by exchangeable aluminum in 1M ammonium chloride as part of the measurement of exchangeable cations. This change in extraction solution reduced the analysis time for exchangeable aluminum while retaining similar experimental conditions. The quantity of mineral soil used in the exchangeable cation analyses was increased relative to the extraction solution which facilitated instrumental analysis. The amount of cellulose filter pulp used in extractions was decreased and a pulp prewash step was added to reduce contamination by exchangeable cations in the pulp material. The determination of extractable cations in 0.002M calcium chloride using a mechanical extractor was changed to an overnight extraction using a mechanical shaker. Also, pH was measured on this extract rather than on a separate extract as used in previous surveys. Total carbon, nitrogen, and sulfur were analyzed by a single laboratory in response to the Mid-Appalachian survey QA requirements for tighter measurement quality and the specialized nature of the analytical instrumentation required for these analyses.

An effort was made to use measurement quality samples in the field, at the preparation laboratory, and at the analytical laboratories in such a way as to provide optimal real-time control and evaluation of data quality. Of particular importance was the addition of field audit samples at the sampling phase to allow the estimation of sampling and system-wide measurement uncertainties. The statistical approach in the Mid-Appalachian survey made use of a balanced hierarchical design that allowed the various components of measurement uncertainty to be estimated with respect to the larger population uncertainty. A step function technique was developed by the QA staff to evaluate data quality in terms of predefined objectives and in relation to the routine sample data.

A Laboratory Entry and Verification Information System (LEVIS) was developed for use by the QA staff and the analytical laboratories. The LEVIS program facilitated the entry, edit, and review of raw data and the calculation of final data values. The program also performed verification checks for the measurement quality samples and produced QC summary reports.

Many significant changes in the batch acceptance criteria were initiated. Among them were the tightening of contract-required detection limits and precision requirements. Several new measurement quality samples were introduced to check both precision and accuracy. Acceptable accuracy windows for laboratory audit samples were established and used as contractual requirements for the laboratories. A template was also developed by the QA staff to assist in setting major and minor flags, and helped to eliminate the subjectivity present in the previous DDRP surveys in regard to reanalysis requests.

Data Quality Assessment

The quality assurance (QA) program for soil sampling, sample preparation, and sample analysis were designed to satisfy measurement quality objectives (MQOs) for the resulting data and to assess the variability of sampling, preparation, and analytical performance. The MQOs for this survey were primarily directed toward the attributes of detectability, precision, accuracy, and completeness. Representativeness and comparability of the data were also assessed, although quantitative MQOs were not imposed.

Detectability

The instrument detection limit is the lowest value that an analytical instrument can reliably detect above instrument background concentrations. Acceptable initial instrument detection limits were established prior to any sample analysis and subsequent values were determined and reported on a batch-by-batch basis. Contracts with the analytical laboratories specified maximum allowable instrument detection limits and, if a reported batch detection limit was invalid, the batch was reanalyzed for that parameter. Secondary checks on the reliability of the instrument detection limits were made using independently determined values.

System detection limits were estimated using low concentration field audit samples which reflected the uncertainty introduced during soil sampling, preparation, extraction, and analysis. These limits allowed data users to identify soil samples which had a measured concentration that was statistically different from the reagent or calibration blanks.

Precision

Precision is the level of agreement among multiple measurements of the same soil characteristic. Measurement imprecision is distinct from the overall variability in the population itself. Determination of measurement imprecision and its sources in the Mid-Appalachian soil survey relied strongly on analysis of the measurement quality samples and was a function of the intralaboratory within-batch precision MQOs defined in the QA Plan. Overall variability stemming from measurement and population sources was estimated from the routine data.

The precision MQOs were characterized by a two-tiered assessment system. Below a specific concentration, called the "knot", precision was defined as an absolute standard deviation in parameter reporting units; above the knot, precision was defined as a percent relative standard deviation. To address the issue of concentration-dependent variance, the range of soil analyte concentrations was partitioned into appropriate intervals within which the error variance was relatively constant. A step function was fitted across the intervals to represent the error variance for the entire concentration range. Different step functions were used to assess variability in selected measurement quality samples, and variability in the population of routine soil samples collected was also estimated.

Accuracy

Accuracy is the level of agreement between an observed value and the "true" value of a soil characteristic. Data from the laboratory natural audit samples were used to estimate analytical accuracy and data from the field natural audit samples were used to assess accuracy from a system-wide measurement perspective. Each audit sample type was assigned a range of acceptable values for each parameter in the form of an accuracy window, which was derived from an MQO-based confidence interval placed around a weighted estimate of the mean calculated using analytical data from the previous DDRP surveys.

The three aspects of accuracy investigated were bias, laboratory differences, and laboratory trends. Analytical bias was considered to be the quantitative measure of accuracy used in the estimation of measurement uncertainty. Laboratory differences were assessed in relation to known reference values and, in conjunction with laboratory trends, served as quantitative and qualitative evaluations of analytical laboratory performance.

Representativeness

The representativeness objectives of the survey were qualitative and quantitative in nature. The general objectives were that: (1) the soil pedons sampled by the field sampling crews be representative of the soil sampling class characteristics, (2) the samples that were collected be homogenized and subsampled properly by the preparation laboratory personnel, and (3) the field duplicate samples adequately represent the range and frequency distribution of analyte concentrations found in the routine samples.

Completeness

The completeness objectives of the survey were to ensure that: (1) all pedons designated for sampling were actually sampled, (2) all samples received by the preparation laboratory were processed, and (3) all samples received by the analytical laboratories were analyzed and that 90 percent or more of the required measurements were made on all of the samples.

Comparability

Comparability of data from the three DDRP surveys was treated as a complex issue having several levels of detail which should be considered. Level 1 comparability was established on the basis of statistical evaluation methods, measurement quality samples, and the sample collection, preparation, and analysis methods used. Level 2 comparability was established by the acceptability and useability of the verified data bases as defined by the data users. Level 3 comparability allowed the direct quantitative comparison of data for each parameter of interest.

Uncertainty Estimates

The term "uncertainty" was used to describe the sum of all quantifiable sources of error associated with a given phase of the measurement system or in the sample population. Uncertainty estimates, or delta values, were calculated for each parameter using the square root of the sum of the within- and between-batch variances and squared bias term. Four delta values were calculated for each parameter. The $delta_1$ values represent analytical laboratory uncertainty and were estimated using the low-range laboratory audit samples. The $delta_2$ values represent the confounded uncertainty of sample preparation and analysis, and were estimated using the preparation duplicates. The $delta_3$ values represent the confounded overall measurement uncertainty of field sampling, sample preparation, and sample analysis, and were estimated using the field duplicates. The $delta_4$ values represent uncertainty due to the spatial heterogeneity of the routine sample population confounded with the overall measurement uncertainty of field sampling, sample preparation, and sample analysis, and were estimated using the sampling class/horizon groups of routine samples. The sampling class/horizon groups refer to configurations of the samples that were believed to have similar physical and chemical properties in relation to soil responses to acid deposition.

Quality Evaluation and Quality Control Samples

Quality evaluation (QE) samples were used to assess overall measurement uncertainty and to provide an independent check on the quality control (QC) procedures. The QE samples were known to the QA staff but were either blind or double-blind to the sampling crews and preparation or analytical laboratory personnel. Six types of QE samples were used in the Mid-Appalachian soil survey: (1) field duplicates (soil samples were collected by each sampling crew from one horizon of every third pedon sampled and were placed randomly in the sample batch with the other samples from the same pedon); (2) field audits (duplicate mineral soil samples or triplicate organic soil samples were sent by the QA staff to the sampling crews for processing as if they were routine samples); (3) low-range field audits (low concentration mineral soil samples were sent with the field audits to the sampling crews by the QA staff); (4) preparation duplicates (a pair of preparation duplicates, one split from the field duplicate sample and one split from its associated routine sample, was created at the preparation laboratory and placed randomly in the sample batch); (5) laboratory audits (duplicate mineral soil samples or triplicate organic soil samples, identical to the field audits were sent by the QA staff to the preparation laboratory for inclusion in each batch); and (6) low-range laboratory audits (low concentration mineral soil samples identical to the low-range field audits were sent to the preparation laboratory by the QA staff for inclusion with each mineral soil batch).

The composition of QC samples was known to the analyst and the analytical results from each laboratory were required to satisfy the batch acceptance criteria as the samples were analyzed. Immediate feedback on the functioning of the analytical system allowed sample processing and analytical deficiencies to be resolved quickly, resulting in minimal error form these sources. Nine types of QC samples were used in the Mid-Appalachian soil survey: (1) QC audit samples were used to control bias and reduce between-laboratory and between-batch measurement uncertainty; (2) analytical duplicates were used to control analytical within-batch precision; (3) calibration blanks were used as a check for sample contamination, analytical carryover effects, and baseline drift in the analytical instrument immediately after calibration; (4) reagent blanks served as a check for reagent contamination; (5) QC check samples served as a check on the accuracy and consistency of the instrument calibration throughout the sample batch analysis; (6) detection limit QC check samples eliminated the necessity of determining the detection limit every day and allowed accuracy to be estimated at the low end of the calibration range; (7) matrix spikes were used to determine the sample matrix effect on analytical measurements; (8) adsorption spike solutions served as a check for reagent contamination; and (9) ion chromatography resolution samples were used to provide evidence of acceptable peak separation for the sulfate analyses.

In addition to the use of QC samples for quality control, technical system audits, or on-site evaluations were also conducted. Each analytical laboratory underwent an audit after successfully analyzing a set of performance evaluation samples prior to receiving a contract. Second-round audits were performed after each laboratory had completed most of the analyses on two sample batches. During third-round auditing, two laboratories underwent two additional audits. The third laboratory underwent only one additional audit.

Data Verification

The analytical laboratories and the QA staff used LEVIS for data verification. Phase one of the LEVIS program included the data entry component and two verification components. The analytical laboratories entered and evaluated data as it was produced using a QC summary report of batch data characteristics and sixteen soil chemistry relationships. The data were then transferred to the central computer at EMSL-LV. The QA staff evaluated preliminary and formally submitted batches from the analytical laboratories using precision and accuracy windows which were checked by LEVIS. The LEVIS program flagged data which did not meet the MQOs. Following the initial data evaluation for a batch, the QA staff prepared a summary document of all flagged parameters, indicating whether a flag originated from an unacceptable value for the QC, chemistry, precision, or accuracy criteria. The number and severity of the flags for each parameter were checked using the QA reanalysis template to determine if reanalysis was required.

After completion and receipt of all final batch data from the analytical laboratories, two internal consistency checks were performed to check for possible outliers in the routine data. A correlation approach was used to assess internal consistency in which the coefficients of determination were obtained by performing weighted linear regressions. From the regressions, studentized residuals and difference of fit statistics were calculated to identify extreme data values that could be considered outliers. Approximately 3 percent of the data underwent confirmation using this consistency check. The second internal consistency check used the data structured into a pedon/horizon data set using the original soil profile sequence. Data for each pedon were visually scanned by soil scientists for consistency of the parameter values from one horizon to the next. Approximately 2 percent of the data underwent confirmation using this consistency check.

Data Management

The field sampling and sample preparation data were entered into SAS-AF™ raw data files on personal computers at EMSL-LV. The analytical data were entered into LEVIS on personal computers located at the laboratories. Data verification was accomplished by a systematic evaluation of completeness, precision, internal consistency, and coding accuracy. Apparent discrepancies were appended with flags unless they could be corrected. After verification was complete, the data bases were frozen and sent to the Oak Ridge National Laboratory in Tennessee to undergo validation in cooperation with personnel at the EPA Environmental Research Laboratory at Corvallis, Oregon, and at EMSL-LV. The validation procedures included a specific assessment of outlying data points for inclusion or omission in validated data sets based on assigned confidence levels.

Results and Discussion

Detectability

The calculated instrument detection limits were less than the contract-required limits for every parameter. Therefore, the MQOs for detectability in the Mid-Appalachian Soil Survey were completely satisfied. System detection limits were used to assess system-wide detectability. Using a criterion of 80 percent or more of the routine sample concentrations exceeding the system detection limits as a basis for assessment, most of the parameters were suitable for all data uses throughout the concentration range. The six exceptions were exchangeable calcium and sodium, iron extracted in calcium chloride or acid oxalate, silicon extracted in acid oxalate, and total sulfur. Data users should use caution when assessing these parameters, as a significant portion of the routine sample concentrations were less than the corresponding system detection limits and may be difficult to distinguish in regard to overall system detection.

Precision

The analytical within-batch precision objectives were satisfied for most of the parameters. Occasionally, an objective was not satisfied for an upper or lower tier of a parameter. When the two tiers were pooled over the total concentration range for each of the parameter groups, a precision index showed that all parameter groups satisfied the "overall" precision objectives.

The precision of the preparation duplicates was about the same, on the average, as the laboratory audit samples and satisfied the MQOs except for iron in acid oxalate. This indicates that the preparation laboratory performed very well in subsampling the bulk soil samples. For the field duplicates, only a few parameters exceeded the precision objectives. In addition, the relatively low precision for the field duplicates for some parameter groups suggests that the component of error from soil sampling, which includes spatial heterogeneity within the sampled horizons, is a large portion of the data collection error.

Accuracy

Accuracy in the Mid-Appalachian soil survey was evaluated by estimating analytical bias with respect to a reference value, defined as the mean of an accuracy window for a given parameter. Laboratory differences and trends were assessed by comparing mean values for the laboratories, combined across audit samples, to the pooled reference values.

Analytical bias was negligible when compared with the system detection limit for all parameters for which system detection limits where established. The only case of significant bias occurred for the cation exchange capacity in ammonium acetate for the two laboratories which used the titration procedure. Bias values for the two newly-established parameters for the Mid-Appalachian survey, i.e., aluminum in ammonium chloride and silicon in acid oxalate, were both much less than their respective detection limits. The percentage of observations that were outside the respective accuracy windows and the magnitude of their contribution to the overall bias estimates were also calculated. The results show a very wide range in the ratios of bias for values outside the window compared to the total analytical bias. Except for total sulfur, every parameter had fewer than 20 percent of its values outside the accuracy windows. Although the percentage of samples outside the window for total sulfur was high, the contribution to overall bias was relatively low. Only 22 percent of the parameters had values outside the window that contributed more than one-third to the bias.

Approximately 54 percent of the parameters showed significant laboratory differences by Scheffe's pairwise comparison test. Only four parameters (total silt, pH in 0.002M calcium chloride, cation exchange capacity in ammonium acetate, and silicon in acid oxalate) showed all three laboratories to be significantly different from each other. There were no general trends for any specific laboratory for most of the parameter groups. For the cations in calcium chloride, however, Laboratory 2 was significantly different from the other laboratories in all cases shown and Laboratory 4 was significantly lower for the sulfate isotherm parameters than the other laboratories in the four cases that showed differences.

Moving averages of the laboratory audit samples were plotted to identify situations when a particular laboratory showed an upward or downward trend over time for a given parameter. Generally, the trends did not show extreme divergence with respect to the accuracy window acceptance criteria. However, certain data users may find the trends to be noteworthy for a specific data analysis.

No single laboratory was consistently superior to the others for all parameters or parameter groups regarding low differences. Each laboratory appears to have individual strengths for specific analytical methods. This is probably a reflection of the combination of experience, instrumentation, and laboratory management practices within each laboratory, resulting in a patchwork of differences on a parameter group basis.

Representativeness

All pedons sampled were within the range of morphological characteristics outlined in their respective sampling classes. The homogenization and subsampling procedures at the preparation laboratory produced representative analytical soil samples of known and accepted quality. Overall precision for the preparation duplicates was approximately equivalent to that of the laboratory audit samples, hence, the procedures were shown to be suitable for creating representative subsamples.

The analyte concentrations in the field duplicates generally were representative of the range and frequency distribution of routine sample concentrations. Analyte concentrations in the preparation duplicates were generally representative of the corresponding field duplicates. The audit samples, as expected, were usually representative only of the overall range of data from the routine samples.

Completeness

Sampling of the specified pedons had a completeness level of 100 percent, and processing was accomplished for 100 percent of the field samples satisfying the sample receipt criteria at the preparation laboratory. Analytical completeness in the verified data base was 100 percent for all parameters. Sufficient validated data were generated to make conclusions for each parameter in the Mid-Appalachian survey data bases, with a completeness level of 98 percent or higher for all parameters. Data qualifiers, or flags, for completeness were inserted in the data base to indicate any missing values.

Comparability

The statistical methods were comparable among the three DDRP surveys. Additional audit samples were used to optimize QE and QC activities in the Mid-Appalachian survey although they did not directly affect the comparability of the data from the surveys.

In most cases the sampling, preparation and analytical methods and protocols for the three surveys were comparable, although there were several parameter protocol modifications in the Mid-

Appalachian survey. The only modification which may affect comparability was the change of aluminum extractant from 1M potassium chloride to 1M ammonium chloride.

As a result of more stringent MQOs in the Mid-Appalachian survey, overall measurement quality generally was better in the Mid-Appalachian data bases. Therefore, it is possible that some of the Northeastern region and Southern Blue Ridge Province data may not be suitable for the same data analysis procedures performed on the Mid-Appalachian data without some form of caveat. Two examples are the organic soil sulfate isotherm data and the specific surface data from the Northeastern and Southern Blue Ridge Province surveys which are generally considered to be suspect by data users.

Significant differences among the surveys were identified using the median-range, mineral soil audit sample common to the three surveys. Only nine parameters showed differences among surveys at the .01 significance level. Although 82 percent of the parameters common to all three surveys were not significantly different at this level across surveys, data users should exercise caution when using data from the nine parameters exhibiting significant differences.

As part of the DDRP, an interlaboratory methods comparison study was conducted which compared soil analysis data from two laboratories using the DDRP methods to 16 statistically randomly-chosen independent laboratories using their own methods which were similar, but not identical to, the DDRP methods. The results of the study show the DDRP data to be comparable with data from the independent laboratories.

Uncertainty Estimates

Within-batch imprecision estimates increased, as expected, from analytical (delta$_1$ values) to sample preparation (delta$_2$ values) to field sampling (delta$_3$ values) to sampling class/horizon groups (delta$_4$ values). The between-batch precision estimates were generally low.

The overall measurement uncertainty in the routine samples was based on the delta$_3$ values which were estimated from the field duplicate samples. The delta$_3$ values, in relation to the associated delta$_4$ values, were used to provide the data users with a basis for assessing the contribution of the measurement system to the data uncertainty. Using this procedure, measurement uncertainty was negligible for 90 percent of the parameters measured) of the data.

Conclusions and Recommendations

As a result of previous conclusions and recommendations from the DDRP Northeastern and Southern Blue Ridge Province surveys, a number of improvements were made in the quality assurance program for the Mid-Appalachian survey. The quality assurance data are presented in a manner considered to be the most appropriate for use by the primary data users. The data quality evaluation procedures and the report format resulted from regular interactions with the data users, and the assessment by several external reviewers. Each user has a subjective concept of data quality as well as a knowledge of the specific level of data quality required for his/her own use. The users are therefore encouraged to become familiar with the text, figures, and tables to facilitate the identification of data satisfying their specific requirements.

The consolidation of sample preparation facilities at a single laboratory facilitated quality assurance of the samples from the field sampling through the sample analysis phase. The separation into different batches of mineral and organic samples should be continued. In addition, measurement quality samples should continue to be distributed among batches and analytical laboratories in such a way as to provide a balanced design for assessment purposes.

The use of a computerized data entry and verification system which allowed the calculation of final data values and produced a list of flags and data entry errors for each sample batch greatly facilitated the verification and reanalysis decision-making process. A similar program should be tailored for each future survey, with the addition of a method that will identify and confirm outlying data points for real-time control purposes.

Considerable effort was expended throughout the three surveys to improve detectability of various parameters and significant improvement was made for the exchangeable cations and sulfur parameters. Additional methods research is needed to improve detectability further. In addition, both instrument and system-wide detectability should be defined in the MQOs. As part of the implementation of such MQOs, it is recommended that low concentration audit samples, entered into the system during the sampling phase, continue to be utilized as substitutes for soil blank samples.

The precision results indicate that the analytical within-batch precision objectives were satisfied in most cases. Occasionally an objective was not satisfied for an upper or lower tier of a parameter. It is recommended that the lower and upper tier precision objectives for exchangeable aluminum in ammonium chloride and extractable silicon in acid oxalate be modified as described in the report. The preparation and field duplicate samples generally satisfied the precision objectives.

Audit sample accuracy windows were developed for use in the Mid-Appalachian survey from data collected in the previous two surveys. The use of a quality control audit sample should be continued in future surveys. In addition liquid audit samples should be incorporated into the quality assurance program and be used to differentiate soil extraction error from instrument error. Emphasis should be placed on the use of audit sample control charts by the QA staff to identify abnormal scatter outside the accuracy windows during the batch analysis.

No single laboratory was consistently superior to the others for all parameters or parameter groups. To control interlaboratory differences in future surveys, it is recommended to continue the selection of a specific laboratory to perform analysis on a parameter basis for those parameters or parameter groups that reveal inherently high differences of where specialized instrumentation is used, e.g., total elemental analysis. Also, a stringent performance evaluation process should be continued to select quality contract analytical laboratories.

Data comparability across the three surveys was generally good. It is recommended, however, that a methods comparison be performed for the two soil extraction methods used for exchangeable aluminum, i.e., 1M ammonium chloride and 1M potassium chloride.

The step function statistical approach has been shown to be an effective procedure for evaluating measurement quality issues in environmental data spanning a wide concentration range. It is recommended that additional research and development be undertaken to identify an optimal step function procedure that is fully compatible with the measurement quality sample design.

Section 1

Introduction

This report serves as documentation of quality assurance (QA) activities that were undertaken in the physical and chemical analysis of soils collected during a major soil characterization effort conducted in the Mid-Appalachian region of the United States. Section 1 provides overviews of the project and the survey work that was performed. The primary participants are outlined and the analytical parameters measured in the survey are described.

Project Overview

The effects of acidic deposition on freshwater ecosystems have been the subject of intensive research during the 1980s. The U.S. Environmental Protection Agency (EPA) recently completed the National Surface Water Survey (NSWS) of the lakes and streams of the United States considered to be most vulnerable to acidic deposition, i.e., those with the lowest acid neutralizing capacity (ANC), as described in Linthurst et al. (1986) and Kaufmann et al. (1988). Analysis of the water chemistry data from the NSWS and other sources in conjunction with temporal and spatial atmospheric deposition data indicates that long-term deposition of sulfur-containing compounds originating from the combustion of fossil fuels has decreased the ANC of some surface waters in eastern North America (Altshuller and Linthurst, 1984; NAS, 1986). The movement of sulfate and other mobile anions through watershed soils and associated cation leaching are the most widely accepted mechanisms of this acidification process (Galloway et al., 1983; Driscoll and Newton, 1985).

Given that acidification of some surface waters has occurred, critical scientific and policy questions focus on whether acidification is continuing in the regions of concern, whether it is just beginning in other regions, how extensive the effects might become, and over what time scales effects might occur. The EPA is addressing these questions through the activities of the Direct/Delayed Response Project (DDRP). The DDRP is being conducted as part of the EPA Aquatic Effects Research Program (AERP) under the congressionally mandated National Acid Precipitation Assessment Program (NAPAP) as described in Church et al. (1989). The overall purpose of the DDRP is to characterize geographic regions of the United States by predicting the long-term response of watersheds and surface waters to acidic deposition. The DDRP draws its name from the consideration of whether acidification might be immediate, i.e., "direct", or would lag in time, i.e., "delayed", because of soil buffering characteristics.

Recent trend analyses have indicated that the rate of sulfur deposition is slowly declining in the northeastern United States but is increasing in the southeastern United States. If a "direct" response exists between sulfur deposition and surface water alkalinity, the extent of current effects on surface water probably would not change much at current levels of deposition, and conditions would improve as the levels of deposition decline. If surface water chemistry changes in a "delayed" manner, e.g., due to chemical changes in the watershed, future changes in water chemistry (even with current or declining rates of deposition) become difficult to predict. This range of potential effects has clear and significant implications for public policy decisions on sulfur emissions control strategies.

The DDRP was not established to identify the exact mechanisms and processes of surface water acidification; rather, the principal mandate was to make regional projections of future effects of sulfur deposition on long-term surface water chemistry based on the best available data and most widely accepted hypotheses of the acidification process. Detailed investigations into processes of soil and surface water acidification are being conducted as part of other projects within the AERP and NAPAP (USEPA, 1989).

Although surface waters can be affected by acidic deposition originating from emissions many miles distant, the concept of the watershed as a unit is critical in understanding current and future aquatic effects. Indeed, for drainage lake and reservoir systems in the Northeast, Upper Midwest, and Southern Blue Ridge regions, most ANC production occurs as a result of biogeochemical processes within the surrounding watershed (Shaffer et al., 1988; Shaffer and Church, 1989). Initially, the use of existing regional soils data was considered for the DDRP analyses. Existing soils data bases, however, were limited with respect to their application to surface water acidification issues. First, such data are available primarily from lowland agricultural regions, whereas surface water acidification occurs principally in relatively undisturbed upland systems. Second, such data bases generally do not include a number of key variables relevant to soil chemical interactions with acidic deposition. Therefore, three major soil surveys were specified to aid in the creation of new regional soils data bases for the DDRP (Lee et al., 1989). The surveys were designed to allow specific soil types to be linked with the existing NSWS data bases that describe the chemistry of low ANC lakes and streams.

The three DDRP surveys shown in Figure 1-1 focused on regions of the United States within which sensitive surface water systems were known to exist. Nonsensitive systems were also known to exist in these regions. The Northeastern (NE) Soil Survey was conducted in 1985 in the states of Maine, New Hampshire, Vermont, Massachusetts, Connecticut, Rhode Island, New York, and portions of Pennsylvania. The Southern Blue Ridge Province (SBRP) Soil Survey was conducted in 1986 in portions of Virginia, Tennessee, North Carolina, South Carolina, and Georgia. This report focuses on the Mid-Appalachian Soil Survey (MASS) which was conducted in 1988 in portions of Pennsylvania, Virginia, and West Virginia. Surface water acidification in these regions was studied during the Eastern Lakes Survey in 1984 and in the National Stream Survey, Phase I, in 1985.

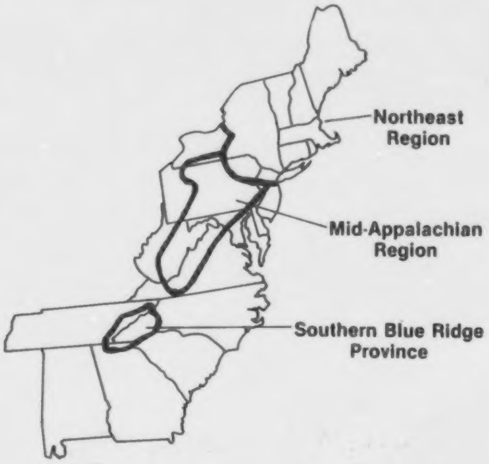


Figure 1-1. Regional Surveys of the Direct/Delayed Response Project (from Lee et al., 1989)

The four specific goals of the DDRP are to: (1) characterize the variability of soil and watershed attributes across these regions, (2) determine which soil and watershed characteristics are most strongly related to surface water chemistry, (3) estimate the relative importance of key watershed processes in controlling surface water chemistry across the regions of concern, and (4) classify the sample of watersheds with regard to their response characteristics and extrapolate the results from the sample of watersheds to the regions of concern (Church et al., 1989). A wide variety of data sources and methods of analysis are used to address the DDRP objectives. In addition to the data collected during the surveys, other sources of information include the following data bases:

- National Surface Water Survey (NSWS) [water chemistry data],
- Acid Deposition Data Network (ADDNET), including GEOECOLOGY [atmospheric precipitation chemistry data],
- Soil Conservation Service (SCS) Soils-5 [soil physical and chemical data],

- Topographic and Acid Deposition System (ADS) [total sulfur deposition data], and
- U.S. Geological Survey [runoff data].

Data from EPA long-term monitoring sites, episodic event monitoring sites, and intensively studied watersheds are used in the data analysis. Uncertainty and error propagation estimates are an important part of all levels of analysis (USEPA, 1989).

The DDRP watersheds were selected as a subset of lake and stream systems surveyed in the NSWS (Church, 1989) and were characterized as probability samples to ensure that results could be extrapolated to a specified target population. A series of maps of soils, vegetation, land use, and depth to bedrock were prepared for each DDRP watershed by the United States Department of Agriculture (USDA) Soil Conservation Service (SCS). Soil sampling classes were defined for each DDRP region, and soils selected from these classes were sampled and analyzed for physical and chemical characteristics. Soils were aggregated within sampling classes to develop class means and variances used in representing characteristics, e.g., by mass or area weighting, of the watersheds of interest.

A variety of complementary data analyses are being performed as part of the DDRP, including the statistical evaluation of interrelationships among atmospheric deposition, mapped watershed characteristics, soil chemistry, and current surface water chemistry. The principal goal of these analyses is to verify that the processes and relationships incorporated in the subsequent modeling analyses reasonably represent the systems under study. Watershed retention of atmospherically deposited sulfur is an important consideration, as are the dynamics of sulfur retention via sulfate adsorption by the soils. Also considered are "single-factor" models (Bloom and Grigal, 1985; Reuss and Johnson, 1986) of the influence of acidic deposition on the supply and transport of base cations from soils to surface waters. The purpose of this modeling is to evaluate the potential relative importance of cation exchange as a mediation process for surface water acidification.

Watershed models are used in the DDRP to project future integrated effects of atmospheric sulfur deposition on surface water chemistry. Three models specifically developed to investigate the effects of acidic deposition on watersheds and surface waters are being applied: The Model of Acidification of Groundwater in Catchments (MAGIC) as described by Cosby et al. (1986); the Enhanced Trickle Down (ETD) model as described by Nikolaidis et al. (1988) and Schnoor et al. (1986); and the Integrated Lake-Watershed Acidification Study (ILWAS) model as described by Chen et al. (1983) and Gherini et al. (1985). Projections of changes in annual average surface water chemistry are being made for each region for at least 50 years using two different scenarios of atmospheric sulfur deposition (Church et al., 1989).

Mid-Appalachian Soil Survey

The DDRP technical director had overall responsibility for the MASS. There were five sampling crews, each consisting of three to four soil scientists, that were assigned the task of sampling selected soil pedons. A pedon is a three-dimensional body of soil having lateral dimensions large enough, i.e., 1 to 10 square meters in area, to permit the identification and sampling of its soil horizons, or horizontal soil layers. In each of the 150 soil pedons selected for sampling, all soil horizons were described on a coded field data form. A total of 844 soil horizons from these pedons were sampled in accordance with documented protocols (Appendix A in Kern and Lee, in press). In addition to collecting 5-kilogram routine soil samples, each sampling crew collected one duplicate sample for QA purposes from every third pedon sampled. Details of the soil mapping and sampling activities are contained in a separate QA report (Kern and Lee, in press).

As part of the MASS, a preparation laboratory was established at Las Vegas, Nevada, to facilitate processing of the field-moist bulk soil samples collected by the sampling crews and to perform preliminary analyses on these samples. The samples were prepared in accordance with standard operating procedures (Appendix A in Papp and Van Remortel, in press). The samples were air-dried, disaggregated, and sieved at the laboratory. Field-moist pH, organic matter by loss on ignition, air-dry moisture, and rock fragments in the soil samples were determined, and the samples were subsequently homogenized and subsampled to produce analytical samples. In addition, the bulk density of replicate soil clods and known volume samples collected by the sampling crews was measured. The analytical samples were grouped into batches of approximately 40 samples per batch. Measurement quality samples, including field duplicates, natural audit samples, and preparation duplicates, were placed in each batch for QA purposes. The samples were added to each batch in a random manner and the batches were subsequently distributed among three analytical laboratories contracted by EPA. A detailed account of the preparation laboratory operations is provided in a separate QA report (Papp and Van Remortel, in press).

Soil physical and chemical analyses were conducted according to documented protocols (Blume et al., in press) by three contracted laboratories. These protocols ensured that the soil sample analyses would yield analytical data of known and acceptable quality. The sampling crews and laboratory personnel received training in the protocols for their respective activities, and on-site technical systems audits were conducted of all participants. Frequent communication between QA personnel and laboratory personnel was established to identify, discuss, and resolve issues raised during the survey.

The QA protocols specified for the MASS were used to maintain consistency in the field sampling, sample preparation, and sample analysis. The design of the analytical QA program has an integral effect on the resulting data quality derived from the physical and chemical analyses of the soil samples. Knowledge of the data quality enables potential users to determine if the data satisfy their specific requirements for the data analysis models or other assessments of the physical and chemical data. In addition, the QA program was designed to ensure that the DDRP data are comparable within and across the regions of concern.

Project Staff Responsibilities

A summary of the different DDRP staff responsibilities at each cooperating EPA laboratory is provided below.

Environmental Research Laboratory, Corvallis, Oregon (ERL-C)

The DDRP staff at ERL-C is active in all aspects of the DDRP soil surveys. Responsibilities of the personnel for the MASS include:

- developing the experimental design and QA oversight for soil mapping and sampling,
- analyzing, validating, and interpreting data,
- preparing progress reports (periodic and final reports with contributions from other laboratories relative to their responsibilities),
- assessing and resolving all science-related issues (jointly with other laboratories),
- preparing QA data reports for soil mapping, sampling operations, and data analysis, and
- coordinating survey activities with NAPAP management staff.

Environmental Monitoring Systems Laboratory, Las Vegas, Nevada (EMSL-LV)

The DDRP staff at EMSL-LV has expertise in matters relating to QA implementation, logistics, and analytical services. The responsibilities of the personnel at this laboratory include:

- developing and implementing the QA project plan, methodology, and standard operating procedures for soil sample preparation and analysis,
- coordinating logistical support and equipment disbursement for field and preparation laboratory operations,
- developing and implementing the data verification and management procedures for soil sampling, preparation, and analysis (jointly with other laboratories),
- analyzing and interpreting data (jointly with ERL-C),
- preparing QA data reports for preparation laboratory and analytical laboratory operations, and
- resolving issues pertaining to laboratory QA, logistics, and analytical services.

Primary Cooperators

The use of federal interagency agreements by EPA allowed the DDRP to engage the support of several organizations that have expertise in areas of importance to the project, as outlined below.

Oak Ridge National Laboratory, Oak Ridge, Tennessee (ORNL)

The DDRP staff at ORNL has expertise in managing, manipulating, and restructuring large data bases to satisfy data analysis needs. The ERL-C staff oversees the activities of ORNL for the following responsibilities:

- developing and maintaining a data base management system (jointly with other laboratories),
- preparing computer-generated summary tables, statistics, and graphics for reports, and
- assisting with data validation and interpretation activities.

Soil Conservation Service (SCS)

The SCS has expertise in soil mapping and characterization on a national scale. Under the guidance of the DDRP staff at ERL-C, the SCS has the responsibility for:

- soil mapping of the MASS watersheds,
- field site selection and characterization, and
- soil sampling of selected pedons.

Organization of the Report

This document has been organized into four main sections. Section 1 provides an overview of the MASS objectives and analytical parameters. Section 2 describes the implementation of the overall QA program, its relation to data quality assessment, and the use of measurement quality samples during the various stages of data collection and verification. Section 3 provides the data quality results and discussion for the analytical parameters measured in the survey. Data quality achievements in relation to objectives established at the beginning of the survey are evaluated. Section 4 addresses the conclusions and recommendations that have been generated from these findings, particularly in regard to issues of concern for sample analysis, improvement in QA design, and suggestions for QA efforts in future surveys. Throughout the report, data quality is described in terms of detectability, precision, accuracy, representativeness, completeness, and comparability.

Description of Parameter Groups

The DDRP QA staff organized the 50 analytical parameters into nine groups and subsequently evaluated each group independently according to the objectives specified for the survey. The nine parameter groups are briefly summarized below:

(1) Moisture and Particle Size Analysis (eleven parameters) -- The air-dry soil moisture content is determined in order to define all subsequent aliquots on an oven-dry weight basis. Particle size analysis is performed on the less than 2-millimeter size fractions of mineral soils for characterization and classification purposes. (Note: the 2-20 mm fraction rock fragments were determined at the preparation laboratory).

(2) Soil pH (three parameters) -- The pH is a measure of free hydrogen ion activity expressed as a negative logarithm. The pH measurements are determined in three soil suspensions: deionized water and two different strengths of calcium chloride solution. The deionized water suspension is universally used in soil laboratories, and the calcium chloride suspension is widely used to address the effects of naturally-occuring salts on pH.

(3) Exchangeable Cations in Ammonium Chloride (five parameters) -- The exchangeable cations (calcium, magnesium, potassium, sodium, and aluminum) are extracted with an unbuffered ammonium chloride solution during the cation exchange capacity (CEC) determinations. These cations, with the exception of aluminum, represent the soil base cations and can be used in the calculation of percent base saturation of the soil and in defining selectivity coefficients and cation pools for the DDRP models.

(4) Exchangeable Cations in Ammonium Acetate (four parameters) -- The exchangeable cations (calcium, magnesium, potassium, and sodium) are extracted with a pH 7.0 buffered ammonium acetate solution during the CEC determinations. These cations can be used in the calculation of percent base saturation of the soil and in defining selectivity

coefficients and cation pools for the DDRP models.

(5) Cation Exchange Capacity and Exchangeable Acidity (three parameters) -- The CEC indicates the ability of a soil to adsorb cations, especially the exchangeable base cations mentioned above. The CEC is highly correlated with the buffering capacity of the soil. Two saturating solutions for the exchangeable cation component of CEC are used: a pH 7.0 buffered ammonium acetate solution for the cation component of "total" CEC, and an unbuffered ammonium chloride solution as the cation component of "effective" CEC at the natural pH of the soil. Exchangeable acidity measures the exchangeable hydrogen ions that are held in the inorganic and organic complexes on the soil particle surfaces, including the hydrogen ions contributed from the aluminum complexes as well as the active acidity in solution. A buffered barium chloride triethanolamine extraction indicates the "total" exchangeable acidity.

(6) Extractable Cations in Calcium Chloride (six parameters) -- Lime potential [pH - 1/2 pCa] is used as an input for certain predictive models. Aluminum potential [3pH - pAl] is another important characteristic for watershed modeling. The soil is extracted with a calcium chloride solution and analyzed for calcium and aluminum concentrations. The magnesium, potassium, sodium, and iron concentrations also are determined and are compared to cation concentrations in other extracts.

(7) Extractable Iron, Aluminum, and Silicon (seven parameters) -- Sulfate adsorption is highly correlated with the presence of iron and aluminum. Each of three extracts estimate a specific iron or aluminum fraction: sodium pyrophosphate estimates organic iron and aluminum; acid oxalate estimates organic iron and aluminum plus sesquioxides; and citrate-dithionite estimates nonsilicate iron and aluminum. Silicon is also determined in the acid oxalate extraction.

(8) Extractable Sulfate and Sulfate Adsorption Isotherms (eight parameters) -- Extractable sulfate is determined in two different extracts: deionized water, which estimates loosely-bound sulfate; and 500 mg P/L as sodium phosphate, which estimates inorganic sulfate held by electrostatic forces or by ligand exchange on the anion exchange sites. The ability of soil to adsorb sulfate is related to anion adsorption capacity. Isotherms are developed by placing soil samples in six magnesium sulfate solutions of different concentrations: 0, 2, 4, 8, 16, and 32 mg S/L. A determination is made of the amount of sulfate remaining in solution after one-hour contact with the soil, and subtraction yields the net sulfate sorption. The isotherms describe sulfate partitioning between solid and solution phases under laboratory conditions and are used to predict changes in sorbed and dissolved sulfate in the soil as a result of altered sulfur inputs.

(9) Total Carbon, Nitrogen, and Sulfur (three parameters) -- Total carbon and nitrogen are closely related to the type and amount of soil organic matter. Total sulfur measures both organic and inorganic sulfur (mostly adsorbed sulfate) in the soil. Ratios of total sulfur are used to characterize sulfur retention in soils and provide a benchmark to monitor future inputs of anthropogenic sulfur.

Description of Parameters

Throughout this document, physical and chemical soil parameters are referenced either by a data-variable or descriptive parameter name. A list of parameters and their corresponding descriptions is given in Table 1-1. The order of the parameters is consistent with their order of presentation in this report.

Table 1-1. Analytical Parameters Measured in the Mid-Appalachian Soil Survey

Parameter	Description of Parameter
MOIST	Air-dry soil moisture measured at the analytical laboratory and expressed as a percentage on an oven-dry weight basis; mineral soils are dried at 105°C, organic soils at 60°C.
SAND	Total sand is the portion of the sample with particle diameter between 0.05 mm and 2.0 mm, and is calculated as the summation of percentages for individual sand fractions: VCOS + COS + MS + FS + VFS.
VCOS	Very coarse sand is the sand fraction between 1.0 mm and 2.0 mm, and is determined by sieving the sand which has been separated from the silt and clay.
COS	Coarse sand is the sand fraction between 0.5 mm and 1.0 mm, and is determined by sieving the sand which has been separated from the silt and clay.
MS	Medium sand is the sand fraction between 0.25 mm and 0.50 mm, and is determined by sieving the sand which has been separated from the silt and clay.
FS	Fine sand is the sand fraction between 0.10 mm and 0.25 mm, and is determined by sieving the sand which has been separated from the silt and clay.
VFS	Very fine sand is the sand fraction between 0.05 mm and 0.10 mm, and is determined by sieving the sand which has been separated from the silt and clay.
SILT	Total silt is the portion of the sample with particle diameter between 0.002 mm and 0.05 mm, and is calculated by subtracting from 100 percent the sum of the total sand and clay.
COSI	Coarse silt is the silt fraction between 0.02 mm and 0.05 mm, and is calculated by subtracting the fine silt fraction from the total silt.
FSI	Fine silt is the silt fraction between 0.002 mm and 0.02 mm; it is determined by pipetting and is calculated by subtracting the clay fraction from the less than 0.02-mm fraction.
CLAY	Total clay is the portion of the sample with particle diameter of less than 0.002 mm; it is determined by pipetting.
PH_H20	pH determined in a deionized water extract using a 1:1 mineral soil to solution ratio or 1:5 organic soil to solution ratio, measured with a pH meter and combination electrode.
PH_002M	pH determined in a 0.002M calcium chloride extract using a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio, measured with a pH meter and combination electrode.
PH_01M	pH determined in a 0.01M calcium chloride extract using a 1:1 mineral soil to solution ratio or 1:5 organic soil to solution ratio, measured with a pH meter and combination electrode.
CA_CL	Exchangeable calcium determined with an unbuffered 1M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
MG_CL	Exchangeable magnesium determined with an unbuffered 1M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
K_CL	Exchangeable potassium determined with an unbuffered 1M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or flame emission spectrometry is specified.
NA_CL	Exchangeable sodium determined with an unbuffered 1M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, or flame emission spectrometry is specified.
AL_CL	Exchangeable aluminum determined with an unbuffered 1M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; inductively coupled plasma atomic emission spectrometry is specified.

(Continued)

Table 1-1. Continued

Parameter	Description of Parameter
CA_OAC	Exchangeable calcium determined with 1M ammonium acetate solution buffered at pH 7.0; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
MG_OAC	Exchangeable magnesium determined with 1M ammonium acetate solution buffered at pH 7.0; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
K_OAC	Exchangeable potassium determined with 1M ammonium acetate solution buffered at pH 7.0; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or flame emission spectrometry is specified.
NA_OAC	Exchangeable sodium determined with 1M ammonium acetate solution buffered at pH 7.0; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, or flame emission spectrometry is specified.
CEC_CL	Cation exchange capacity determined with an unbuffered 1M ammonium chloride solution is the effective CEC which occurs at approximately the field pH when combined with the acidity component; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; samples are analyzed for ammonium content by one of three methods: automated distillation/titration; manual distillation/automated titration; or ammonium displacement/flow injection analysis.
CEC_OAC	Cation exchange capacity determined with 1M ammonium acetate solution buffered at pH 7.0 is the theoretical estimate of the maximum potential CEC for a specific soil when combined with the acidity component; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; samples are analyzed for ammonium content by one of three methods: automated distillation/titration; manual distillation/automated titration; or ammonium displacement/flow injection analysis.
AC_BACL	Total exchangeable acidity determined by titration in a buffered (pH 8.2) barium chloride triethanolamine extraction using an approximately 1:30 soil to solution ratio.
CA_CL2	Extractable calcium determined by a 0.002M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; the calcium is used to calculate lime potential; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
MG_CL2	Extractable magnesium determined by a 0.002M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
K_CL2	Extractable potassium determined by a 0.002M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; atomic absorption spectrometry or flame emission spectrometry is specified.
NA_CL2	Extractable sodium determined by a 0.002M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, or flame emission spectrometry is specified.
FE_CL2	Extractable iron determined by a 0.002M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; inductively coupled plasma atomic emission spectrometry is specified.
AL_CL2	Extractable aluminum determined by a 0.002M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; the aluminum concentration obtained from this procedure is used to calculate aluminum potential; inductively coupled plasma atomic emission spectrometry is specified.
FE_PYP	Extractable iron determined by a 0.1M sodium pyrophosphate extraction using a 1:100 soil to solution ratio; the pyrophosphate extract estimates organically-bound iron; inductively coupled plasma atomic emission spectrometry is specified.

(Continued)

Table 1-1. Continued

Parameter	Description of Parameter
AL_PYP	Extractable aluminum determined by a 0.1M sodium pyrophosphate extraction using a 1:100 soil to solution ratio; the pyrophosphate extract estimates organically-bound aluminum; inductively coupled plasma atomic emission spectrometry is specified.
FE_AO	Extractable iron determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio; the acid oxalate extract estimates organic and amorphous iron oxides; inductively coupled plasma atomic emission spectrometry is specified.
AL_AO	Extractable aluminum determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio; the acid oxalate extract estimates organic and amorphous aluminum oxides; inductively coupled plasma atomic emission spectrometry is specified.
SI_AO	Extractable silicon determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio; inductively coupled plasma atomic emission spectrometry is specified.
FE_CD	Extractable iron determined by a sodium citrate-sodium dithionite extraction using a 1:30 soil to solution ratio; the citrate dithionite extract estimates non-silicate iron; inductively coupled plasma atomic emission spectrometry is specified.
AL_CD	Extractable aluminum determined by a sodium citrate-sodium dithionite extraction using a 1:30 soil to solution ratio; the citrate dithionite extract estimates non-silicate aluminum; inductively coupled plasma atomic emission spectrometry is specified.
SO4_H2O	Extractable sulfate determined with a double deionized water extract; this extraction approximates the sulfate which will readily enter the soil solution and uses a 1:20 mineral soil to solution ratio or 1:40 organic soil to solution ratio; ion chromatography is specified.
SO4_PO4	Extractable sulfate determined with a 0.016M sodium phosphate (500 mg P/L) extract; this extraction approximates the total amount of adsorbed sulfate and uses a 1:20 mineral soil to solution ratio or 1:40 organic soil to solution ratio; ion chromatography is specified.
SO4_0	Sulfate remaining in a 0 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
SO4_2	Sulfate remaining in a 2 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
SO4_4	Sulfate remaining in a 4 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
SO4_8	Sulfate remaining in a 8 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
SO4_16	Sulfate remaining in a 16 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
SO4_32	Sulfate remaining in a 32 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
C_TOT	Total carbon determined by rapid oxidation followed by infrared detection or thermal conductivity detection using an automated CHN analyzer; total carbon can be used to characterize the soil organic matter.
N_TOT	Total nitrogen determined by rapid oxidation followed by infrared detection or thermal conductivity detection using an automated CHN analyzer; total nitrogen can be used to characterize the soil organic matter.
S_TOT	Total sulfur determined by automated sample combustion followed by infrared detection of evolved sulfur dioxide.

Section 2

Quality Assurance Program

Quality assurance may be defined as "a system of activities whose purpose is to provide to the producer or user of a product or service the assurance that it meets defined standards of quality with a stated level of confidence" (Taylor, 1987). The QA program was designed for statistical control to ensure that the MASS data collected were of the highest integrity and that the data quality could be evaluated and documented. These procedures included the preparation of written protocols and manuals describing: (1) soil sampling, preparation, and analysis; (2) application of QA procedures during field and laboratory activities; and (3) verification of the descriptive and analytical data (see Figure 2-1). Specific aspects of the QA program are described in the following subsections.

Quality Assurance Optimization

Due to overlapping verification activities during the DDRP NE and SBRP surveys, there was insufficient time to fully evaluate the NE data in order to optimize the latter survey to produce data of higher quality. However, there was sufficient time available to evaluate the NE and SBRP data before the MASS was implemented. The two primary objectives during the evaluation phase were to identify procedures that could improve data quality and to develop the QA staff operations in such a way as to expedite the survey. An improvement in data quality was necessary because the data users had determined that the data for certain parameters in the NE and SBRP surveys contained more uncertainty than was desirable for their intended use. In order for the MASS data to be available for the 1990 NAPAP assessment, the EMSL-LV operations had to be completed in a significantly shorter timeframe than in the previous surveys.

The subsections below are intended to highlight the major features of optimization applied to the MASS sample preparation and analysis. The discussion is intended only as a summary of the features because additional details are provided in other parts of this section or in supporting documents as referenced.

Consolidated Preparation Laboratory Facility

The NE and SBRP surveys utilized multiple laboratory facilities to perform the necessary sample preparation tasks. These facilities were also used as storage and distribution centers for consumable field sampling supplies. The following difficulties were encountered with multiple preparation facilities:

- the progress of the preparation laboratories was difficult to track, especially concerning sample batch shipment to the analytical laboratories;
- batches were not always sent within a regular timeframe, leading to difficulties in tracking the progress of batch analysis;
- control of possible contamination sources at the different facilities was inconsistent;
- the distribution of samples among sampling crews and laboratories was irregular and unbalanced;
- significant time and expense was required to perform technical systems audits at multiple facilities;
- real-time control of data quality at the laboratories was inconsistent;
- variable air-dry moisture contents in soils occurred due to different geographic locations of laboratories;
- subtle differences in preparation techniques and interpretation of protocols occurred; and

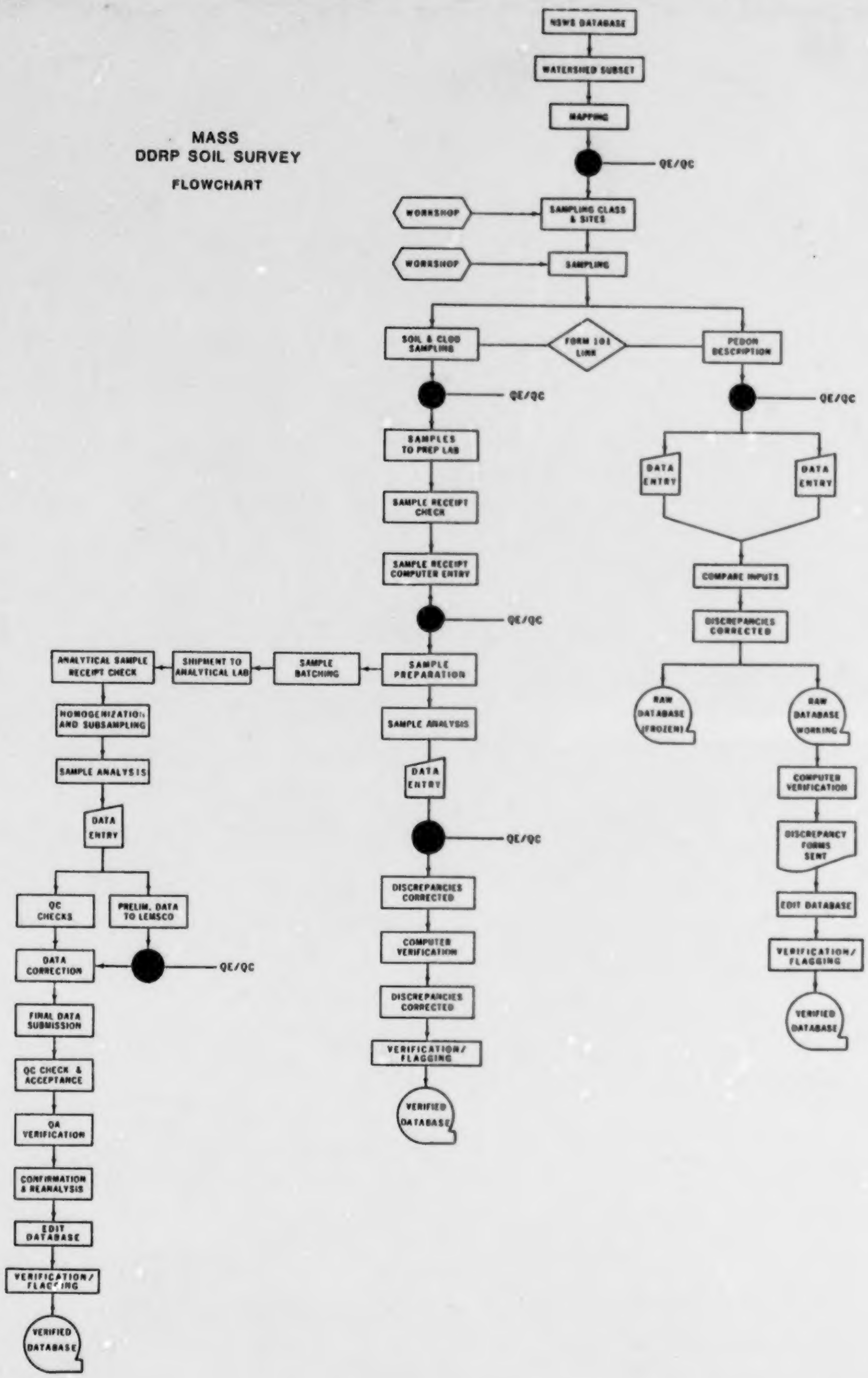


Figure 2-1. Flowchart of verification activities in the Mid-Appalachian Soil Survey.

- some sampling crews acquired an inordinate amount of supplies at the expense of other crews because of unsatisfactory disbursement and control of field equipment and consumable supplies.

The DDRP management team determined that more real-time control of the preparation facilities was necessary. This determination led to the establishment of a single MASS preparation laboratory located in Las Vegas, Nevada, in close proximity to the EMSL-LV QA staff. The consolidation of sample preparation activities allowed:

- rapid and consistent soil drying due to the low relative humidity;
- establishment and consistent adherence to strictly-defined sample preparation protocols;
- the ability to track and control progress at the laboratory on a real-time basis;
- a central control and distribution point for field sampling supplies, thereby alleviating shortages;
- elimination of confounded multi-laboratory measurement uncertainties at the preparation phase;
- better distribution of samples among sampling crews and laboratories;
- advanced controls against sample contamination; and
- minimal time and expense for conducting technical systems audits.

Separation of Mineral and Organic Samples

Previously in the DDRP surveys, organic soil samples were randomly intermingled with mineral soil samples in each batch. For a number of reasons, this practice was modified for the MASS. Organic soil horizons generally have much higher analyte concentrations than mineral soil horizons within a pedon. Organic soil to solution ratios are often quite different than mineral soil to solution ratios for the laboratory analysis of a given parameter. The fluctuation between sequential high and low sample readings on an analytical instrument can produce erroneous data because of a "carryover" effect from the instrument. Also, certain parameters were not required to be analyzed for organic soils.

For the MASS, mineral and organic samples were placed in separate batches. Samples were defined as organic if their organic matter content was 20 percent or more by weight as measured at the preparation laboratory. This enabled the laboratories to perform the instrument calibration and sample analysis within narrower linear dynamic ranges and allowed the QA staff to better assess the quality of data generated by the analyses. As a result of this development, different precision objectives were defined for the mineral and organic batches.

Changes in Parameters and Methods

Several changes in analytical methods and procedures were initiated for the MASS as a result of data quality limitations and recommendations from the NE and SBRP surveys, and from special studies initiated to address concerns raised during those surveys. The changes included:

- Analysis of exchangeable acidity in 1M potassium chloride (AC_KCL) was excluded from the analytical parameters because it was not used in the summation of cations for the calculation of CEC or base saturation in the previous surveys; as a result, the data users recommended replacing the determination of exchangeable aluminum in 1M potassium chloride (AL_KCL) with a determination of exchangeable aluminum in 1M ammonium chloride (AL_CL) as part of the measurement of exchangeable cations; the change reduced the analytical time required to determine exchangeable aluminum while retaining very similar extraction conditions.
- The determination of specific surface was excluded for the MASS sample analysis and no substitute physical determination was recommended; the specified method in the two earlier surveys was ethylene glycol monoethyl ether (EGME), which was a time-consuming method that resulted in widely varying data for the high surface area of the clay fraction in the soil samples.
- Silicon was added to the list of analytical parameters; silicon extracted by acid oxalate (SI_AO) is a measure of amorphous silica, which is a component of the total silicon in the soil; in the previous surveys, X-ray fluorescence was used to measure total silicon in a 10 percent representative subsample of the population of routine soil samples.

- The analytical procedures for the exchangeable cations in both ammonium chloride and ammonium acetate were revised; in the first two surveys it was found that several of the cations were at very low concentrations in many mineral soil samples; in order to increase the concentration of the cations in the extract prior to instrumental analysis, it was recommended that the quantity of mineral soil used in the extraction be increased from 2.5 to 5.0 g.
- The results of a special study included a recommendation that the amount of cellulose filter pulp used in extractions be reduced from 1.0 to 0.5 g; the pulp was found to contain low levels of exchangeable cations and could possibly contribute to the measured cation exchange capacity; the study tested several other materials for possible substitution, but none were found to be superior to the cellulose for all purposes; to minimize possible contamination, however, the procedure for the preparation of the cellulose pulp was revised to include a washing step using hydrochloric acid.
- The determination of extractable cations in 0.002M calcium chloride using a mechanical extractor was changed to an overnight extraction using a mechanical shaker; in addition, PH_002M was determined on this extract rather than on a separate extract used for soil pH in the previous surveys.
- The strength of the triethanolamine solution used for total exchangeable acidity (AC_BACL) was reduced from 0.2M to 0.1M; in addition, the titer strength was reduced from 0.1M to 0.05M hydrochloric acid; these changes were recommended in order to more accurately determine the total acidity in soils having low acidity content.
- The use of vanadium pentoxide as a combustion accelerator was recommended for the determination of C_TOT and N_TOT; this accelerator is used to increase the temperature and, therefore, decrease the reaction time and ensure a more complete combustion; it replaced the formerly used accelerator which was composed of iron chips, granular tin, and copper.

Consolidation of Total Elemental Analysis

For the NE and SBRP surveys, all contract laboratories analyzed total carbon, nitrogen, and sulfur, and reported the results along with the other parameters. Due to the MASS requirements for tighter measurement quality and the specialized nature of the analytical instrumentation, it was recommended by the data users that these three elemental parameters be analyzed by only one carefully selected laboratory. Performance evaluation protocols were written specifically for these analyses, as well as a separate statement of work and special contractual considerations.

Sample Design

One of the conclusions drawn from the two previous DDRP surveys was that the sample design should be more robust and enable more information to be derived from the analysis of measurement quality samples. It was also noted that there were insufficient samples in the batches to assess the effects of the various phases of sample measurement, i.e., sampling, preparation, and analysis, in relation to the system-wide measurement uncertainty. The possibility of contamination introduced through the measurement system was a common concern voiced by reviewers of the DDRP QA program.

For the MASS, an effort was made to use measurement quality samples in the field, at the preparation laboratory, and at the analytical laboratories in such a way as to provide optimal real-time control and assessment of data quality. Of particular importance was the addition of field audit samples at the sampling phase to allow the estimation of sampling and system-wide measurement uncertainties. Data from previous surveys were used to develop ranges of acceptable analyte concentration for the assessment of accuracy. The hierarchical sample design described later in this section and in the QA Plan (Papp et al., 1989) utilized blind and double-blind samples to provide a complete evaluation of the data quality issues.

Statistical Design

A number of design characteristics were investigated during the two previous DDRP surveys, particularly in regard to statistical analysis issues. During the data quality assessment of the NE survey data base, issues were raised regarding concentration dependency of the error variance, mathematical transformation of data, and data reporting criteria. It was eventually decided that the logarithmic transformation technique originally applied to address concentration dependency was not suitable for the requirements of the data users, and that a statistical measure more closely linked to the quality objectives and the routine sample data was needed.

As a result of these findings, the QA staff developed a step function technique (Miah et al., 1989), described later in this section, to evaluate data quality in terms of predefined objectives and in relation to the routine sample data. This approach made use of a balanced hierarchical design that allowed the various components of measurement uncertainty to be estimated with respect to the overall uncertainty in the population of data collected. The information was used to caution data users about those situations where measurement uncertainty is a significant contributor to overall data uncertainty.

Computerized Data Entry and Verification

The most labor-intensive and lengthy operation in the DDRP QA program at EMSL-LV was the verification of analytical data. For the NE and SBRP surveys, the QA staff used hardcopy batch data packages for verification while the data were being entered on personal computers by ORNL staff. Lack of an automated verification program meant that precision estimates and the majority of verification checks were calculated by hand, with a single batch evaluation requiring approximately 100 hours to complete. Therefore, laboratories would not receive affirmation of batch acceptance for a number of weeks after submission. This delay often affected the reanalysis procedure at the analytical laboratories because they did not always have the option to reanalyze the initial extraction solutions and occasionally had to re-extract the soils at the expense of both time and money.

Due to the critical timeframe for delivery of the verified MASS data, a Laboratory Entry and Verification Information System (LEVIS) was developed that could be utilized at the laboratories (see Data Verification). The LEVIS program facilitated the entry, editing, and review of intermediate data and the calculation of final data values for the MASS. The program also performed verification checks for the measurement quality samples and produced summary reports of data quality.

A modem-linked laboratory personal computer was available to facilitate the transfer of preliminary data which were used to evaluate the current status of laboratory operations and data entry. The laboratories delivered the official analytical data to the QA staff in hardcopy and on floppy disks in the LEVIS data base structure. The QA staff performed additional verification checks on a personal computer and the data were reviewed for confirmation/reanalysis requirements. The data generated by batch reanalysis were entered and verified in the same manner.

The LEVIS program greatly improved the timeliness of the verification operation. Complete verification of all quality control (QC), precision, accuracy, and soil chemistry relationship data for a batch of samples was accomplished in approximately four hours. The increased efficiency of the verification process aided in reanalysis because the analytical laboratories were notified in time to reanalyze the existing extracts.

Acceptance Criteria

During the early stages of the DDRP, the QA staff lacked a definitive basis for establishing acceptance criteria because previous studies of this type had not instituted such an intensive QA program. The batch acceptance criteria for the NE survey were based on the abilities of the analytical laboratories to satisfy specific QC requirements, e.g., for reagent blanks, and precision objectives for individual pairs of audit samples and duplicate samples. Nearly identical criteria were used for the SBRP survey. In the absence of established accuracy windows, a subjective "visual" assessment of accuracy was made by the data reviewer using data from previous sample batches. Allowances for deviations from the contractual requirements were somewhat subjective, with few firm protocols established for corrective action. Precision was checked only if sample concentrations were greater than or equal to 10 times the contract-required detection limit (CRDL), and a percent relative standard deviation was the only statistical criterion applied. Failure to satisfy the precision objectives for the laboratory audit samples justified a request for batch reanalysis, while requests for reanalysis on the basis of duplicate sample variability were subjective. The ongoing precision of the duplicate samples was tabulated and if the variability for a specific batch were extremely high, in the judgement of the data reviewer, reanalysis was requested. A series of chemistry relationships were checked and used to encourage the laboratories to check for data reporting errors such as transposed digits. In several instances, batch reanalysis was requested due to the failure of a large, unfixed number of relationship failures in the judgement of the data reviewer. The QA staff began to use reanalysis templates late in the NE survey to aid in standardizing the basis for requesting reanalysis. For the SBRP survey, an additional laboratory audit sample pair was incorporated into each batch to provide a better check of the analytical laboratory precision.

For the MASS, many significant changes in the acceptance criteria were initiated. The CRDLs and precision requirements of the QC samples, described later in this section, were tightened. Additionally, precision was checked on all pairs of measurement quality samples without regard to low concentration values approaching the CRDL. A two-tiered scale was used for precision, where the lower range of concentration was assessed using an absolute standard deviation and the upper range of concentration was assessed using a relative standard deviation.

Several new measurement quality samples were introduced to check both precision and accuracy. Field audit samples were included in each batch to measure system-wide precision components. Accuracy windows for laboratory audit samples were established and used as contractual requirements for the laboratories. Detailed reanalysis templates were developed by the QA staff to assist in setting major and minor flags and to eliminate the subjectivity present in the NE and SBRP surveys in regard to reanalysis requests.

The analytical laboratories were also contractually required to satisfy a larger group of chemistry relationships, with batch reanalysis requested if six or more relationships failed in a single batch. Upon completion of analysis, two types of internal consistency checks were implemented to identify possible outliers and request confirmation of these data or reanalysis of the affected samples.

Selection of Analytical Laboratories

It was determined before the onset of the DDRP surveys that EPA laboratories and the analytical laboratories participating in the EPA Contract Laboratory Program did not have the specific instrumentation nor expertise to conduct the analysis of all required DDRP parameters. Therefore, analytical services were solicited from commercial analytical laboratories, and a laboratory selection process was developed that would objectively evaluate analytical performance to satisfy the data requirements for the DDRP. These requirements had to be clearly and concisely documented in statements of work and the data consistently and objectively evaluated for each laboratory in order to identify those most qualified to perform the analyses.

Statements of Work

The contracting process included the preparation of detailed analytical laboratory statements of work (ALSOWs) which defined the analytical and QA requirements in a contractual format. Two ALSOWs were created, one for general soil analysis (W802498D1) and the other for total elemental soil analysis of carbon, nitrogen, and sulfur (W802621D1). Although the MASS analytical protocols and initial draft of the QA Plan were prepared in the early phases of the planning process, the laboratory methods and data quality requirements had to be presented in a contractual format in order to obtain support services. This process involved careful review of the analytical and logistical requirements, i.e., reporting and QC stipulations, to ensure their clarity in the ALSOW and their ability to be satisfied according to the contract specifications. The analytical laboratories were required to follow the methods exactly as specified in the ALSOW. The project officer was authorized to provide technical clarifications for the contract laboratory, but contractual changes could be made only with the written approval of the EPA contract officer.

An invitation for bid (IFB) was prepared for each ALSOW and subsequently advertised in the *Commerce Business Daily* to solicit analytical support from interested laboratories. It was anticipated that approximately 800 to 1,000 soil samples would be collected in the MASS. A contractor could bid on the analysis of one or more bid lots (40 to 800 soil samples per bid lot for general analysis, 80 to 1,600 samples per bid lot for elemental analysis). Bid lots were specified for delivery to the analytical laboratories at a maximum rate of one batch per week, with each batch containing approximately 40 samples. Delivery of the completed batch data package by the contractor was required within 60 days of sample receipt. Reanalysis was requested of suspect data identified through data quality management activities, and full payment was withheld pending compliance with any such requests. Initial responses to the IFBs were received from 54 laboratories for general analysis and 9 laboratories for elemental analysis.

Performance Evaluations

All interested laboratories received a set of five pre-award performance evaluation (PE) samples. As part of the bid submission package for qualification, these laboratories were required to analyze the PE samples and to report the results within 25 days following sample receipt. The PE samples consisted of four mineral audit samples and one organic audit sample, and were intended to represent the low, medium, and high analyte concentrations expected in the soil samples collected during the survey. Data packages received from each competing laboratory were evaluated and graded on the QC, precision, accuracy, and chemistry relationships of analytical data as well as the quality and completeness of the data package, using the scoring sheet provided in Appendix E of the MASS QA Plan (Papp et al., 1989). This evaluation identified those laboratories that could successfully perform the analyses at the level of quality required for the DDRP. During this stage, 49 laboratories withdrew from the competition for general analysis because of the high number of parameters to be analyzed or the stringent instrument specifications. Also, five laboratories withdrew from the competition for elemental analysis.

Three of the remaining five laboratories that submitted bids for general analysis successfully passed the PE sample evaluation and were visited by EPA technical and contracting representatives who verified the qualifications and capabilities of these laboratories to meet or exceed the contractual requirements. The EPA team determined whether each analytical laboratory had adequate facilities, equipment, personnel, and technical capabilities to analyze large numbers of samples in accordance with the ALSOWs and within the required timeframe of the survey. These visits also provided an opportunity to clarify contractual specifications with laboratory personnel and to identify deficiencies that were observed during the PE phase.

Three of the remaining four laboratories that submitted bids for elemental analysis successfully passed the PE sample evaluation. The laboratory that submitted the most competitive bid was visited by EPA representatives who verified the qualifications and capabilities of this laboratory to meet or exceed the contractual requirements. Had this laboratory not passed the on-site evaluation, the EPA team would have visited the laboratory which submitted the next most competitive bid until a fully qualified laboratory could be identified.

Award of Analytical Contracts

The laboratories that successfully passed both the performance and on-site evaluations were awarded contracts to provide analytical services for the MASS general soil analysis. However, because only one bid lot for the elemental analysis contract was to be awarded, the qualifying laboratory that submitted the most competitive bid and successfully passed the on-site evaluation was subsequently awarded the elemental analysis contract. Coincidentally, this laboratory was also one of the three laboratories that was awarded a contract for general analysis.

In the previous two DDRP surveys, there were four participating analytical laboratories that were described as Laboratories 1, 2, 3, and 4 in the QA reports (Van Remortel et al., 1988; Byers et al., 1989). All four laboratories analyzed samples in the NE survey, while only Laboratories 1, 2, and 3 analyzed samples in the SBRP survey. Three of these same four laboratories were selected for the MASS sample analysis, namely, Laboratories 1, 2, and 4. Laboratory 3 did not submit a bid for either the MASS general or elemental analyses, although the NE and SBRP data from this laboratory are used in many of the comparability discussions in Section 3 of this QA report.

Distribution of Batches

Prior to initiating the routine sample analysis, the analytical methodology was employed in the analysis of three batches containing several replicates of various types of audit samples. One batch was sent to each of the selected analytical laboratories and the resulting data were used only to examine the utility of the batch acceptance criteria and other operations components of the MASS. Subsequently, 27 mineral soil batches and 2 organic soil batches were analyzed among the three laboratories, as outlined in Table 2-1. Organic and mineral soils were placed in separate batches because of the expected wide variability in analyte concentrations.

Table 2-1. Distribution of Batches for General Soil Analysis

Laboratory	Number of batches	Batch code[a]
L1	9	30104[b], 30107, 30110, 30113, 30116, 30119, 30122, 30125[b], 30128
L2	9	30106, 30109, 30112, 30115, 30118, 30121, 30124, 30127, 30130
L4	11	30105, 30108, 30111, 30114, 30117, 30120, 30123, 30126, 30129, 30131[c], 30132[c]

[a] L2 also performed the elemental soil analyses (C_TOT, N_TOT, S_TOT) for all 29 batches.

[b] Batch later retrieved from L1 and sent to L4 for reanalysis of exchangeable calcium and magnesium (coded as batches 39104 and 39125, respectively).

[c] Batch contained only organic samples.

Analytical Laboratory Quality Control

Each analytical laboratory was required to comply with stringent QC requirements during the MASS sample analysis. Specific requirements were stated in the QA Plan (Papp et al., 1989) for sample receipt and storage, use of laboratory protocols, sample homogenization, instrument calibration, data entry, data reporting, and preventive maintenance. These subjects are described in the following sections.

Sample Receipt and Storage

The routine bulk samples were collected from each of the selected soil pedons by five sampling crews. These bulk samples were delivered to a single preparation laboratory located at EMSL-LV, where the samples underwent processing. The laboratory staff prepared two homogenized analytical samples from each air-dried bulk sample: a general analysis sample weighing approximately 450 g and an elemental analysis sample weighing approximately 50 g. All leftover soil was archived in long-term cold storage.

All samples received at each analytical laboratory were checked for sample integrity by a receiving clerk who recorded on the shipping form, DDRP Form 102 (see Appendix K), the date that the samples were received. The sample labels were checked against the form to identify discrepancies. A copy of the form was then sent to the QA manager. If there were any discrepancies or problems, such as sample leakage or insufficient sample volume, the QA manager was notified immediately for instructions. The samples were refrigerated at 4°C as soon as possible after receipt by the laboratory and were kept refrigerated when not undergoing routine analysis. After all analyses were completed, the samples were placed in long-term cold storage to ensure sample integrity in the event that reanalysis was requested.

Laboratory Protocols

The analytical methods and associated protocols used in the MASS were selected to ensure that the resulting data would be comparable with other similar data bases, e.g., the DDRP NE and SBRP data bases. General laboratory QC protocols included the use of trained laboratory personnel, suitable laboratory facilities, appropriate instrumentation with known performance characteristics, and laboratory supplies of sufficient quality and quantity for the specific purpose. The laboratories were occasionally required to use specific manufacturers and models of instruments. Written standard operating procedures, a laboratory QA plan, and a record of in-house samples were required. Control charts, with 99 and 95 percent control limits, were plotted for the QC soil samples and liquid check samples, and were updated daily for each parameter undergoing analysis. The charts were submitted to EMSL-LV upon request at any time during, or immediately following, the survey. On-site technical systems audits ensured that the laboratory protocols and procedures were followed correctly (see Appendix H).

Sample Homogenization

The bulk soil samples processed by the preparation laboratory were air-dried, disaggregated, and sieved to retain the less than 2-mm fraction (Papp and Van Remortel, in press). Analytical samples were prepared by homogenization and subsampling using a closed-bin riffle splitter. Immediately after receiving these samples from the preparation laboratory, the analytical laboratories homogenized each sample by passing the entire sample through a closed-bin riffle splitter five times in succession. After this step, approximately half of the contents of each sample was stored and the other half was used for the analyses. Sample movement in the laboratory, e.g., transport or shaking, was restricted in order to minimize sample segregation by particle size and density. Sample aliquot removal was accomplished by random insertion of a sampling device, e.g., spatula or scoop, into the sample bottle.

Instrument Calibration

For most methods, a calibration curve was established using a minimum of three points within the linear dynamic range of the instrument unless the manufacturer's recommendations specified the use of more than three points within the range. The linear dynamic range was determined by a least squares regression analysis (Steel and Torrie, 1960), and the correlation of concentration and instrument response was required to be 0.99 or higher. The lowest concentration of the calibration standards was required to be not more than 10 times the CRDL, as described later in this section.

The concentrations of standards bracketed the expected range of sample concentrations without exceeding the linear dynamic range, with one exception. Laboratory 4 was allowed to use an upper calibration standard of 2 mg/L Ca^{2+} for calcium extracted during the analysis of CA_CL2, even though sample concentrations may have exceeded the upper calibration limit. This exception was made because this laboratory had been able to demonstrate instrument linearity throughout the range of calcium concentration. However, Laboratory 4 was required to verify linearity by using a 100 mg/L Ca^{2+} (± 5%) standard for each batch. In all other cases, the laboratories diluted and reanalyzed samples if their concentrations exceeded the linear dynamic range.

Data Entry

After all samples in a batch were analyzed for a given parameter, the results were entered on raw data forms and subsequently entered into a specialized computer system using a personal computer supplied to each analytical laboratory by the EPA (see Data Verification). A single-entry system was employed in conjunction with a complete visual data check performed by the laboratory manager prior to formal data submission. The computer system had the ability to produce screens of standardized data forms that allowed entry of sample weights, solution volumes, dilution factors, instrument readings, titrant volumes, and titer acid normalities for routine sample analysis, all with the appropriate predefined number of significant decimal places. Separate data forms or spaces were provided for the QC sample data, and a page was also provided to allow the documentation of any comments concerning the analyses or samples by the laboratory analyst or manager.

Data Reporting

Analytical data were reported according to the protocols specified in the ALSOW (USEPA, 1988). For formal submission of a batch of data, each laboratory was required to provide: (1) a signed cover letter that indicated the date, laboratory name, and batch number being formally submitted; (2) a copy of DDRP Form 102; (3) a floppy disk containing all data files generated; and (4) hard copies of all appropriate data forms. The data contained on the floppy disk and the hard copies were required to be identical or a resubmission was requested following identification and correction of any deficiencies. Each laboratory manager signed a completed data form to indicate that the batch data had been reviewed and that the samples were analyzed exactly as described in the ALSOW. Any deviations from the protocols were required to be documented on the form. Copies of the raw data were submitted upon request of the QA manager; otherwise, all original raw data were retained at the analytical laboratories. The raw data include data system printouts, chromatograms, notebooks, individual data sheets, and control charts.

If data confirmation was requested, i.e., a recheck of suspect data values, the analytical laboratories submitted a completed DDRP Form 500 (see Appendix K) indicating whether the questioned data values were correct. If a correction was made in the data, the laboratory manager made note of the change, initialed the form, and provided an explanation for the change. The correction was made in the data base and an updated data reporting form was generated. Raw data supporting the change were provided upon request of the QA manager. There were no laboratory qualifiers, or tags, reported by the laboratories during the MASS, whereas the reporting of tags was prevalent in the previous DDRP surveys. Instead, any comments relating to the tag definitions in the MASS QA Plan (Papp et al., 1989) were entered as free-form notes on the data reporting forms.

Preventive Maintenance

The analytical laboratories were required to maintain their instruments in good operating condition. Instrument breakdowns or failures were required to be repaired within a reasonable time period and documented in an instrument logbook. Each logbook contained information pertaining to routine maintenance and cleaning, calibration problems, and repairs. If an instrument failed during analysis of a batch, all samples in that batch were reanalyzed following instrument repair and recalibration.

Analytical balances were calibrated at the beginning of each day of use. A balance was considered to be in need of maintenance if the calibration readings exceeded the range of the respective Class S weight at the level of sensitivity required for a particular analysis. A check of the logbooks during the technical systems audits showed that the balances were adequately calibrated during the sample analysis period.

Technical Systems Audits

An exercise which was extremely useful in controlling data quality in the MASS was the technical systems audit, or on-site evaluation, which was conducted to ensure that all laboratories adhered to the protocols in a consistent manner. Each analytical laboratory underwent a minimum of three technical systems audits during the survey. Between audits, frequent communications were maintained between the QA staff and designated laboratory personnel to ensure that each laboratory was satisfying the QC requirements and to make a preliminary evaluation of data quality and laboratory performance. This contact enabled the QA audit team to become familiar with analytical difficulties at the laboratories that were subsequently discussed during audit visits.

The first on-site technical systems audits were performed in September 1988, after each laboratory had successfully analyzed the set of pre-award PE samples. The QA manager and the QA soil chemist evaluated each of the laboratory functions that were pertinent to the analyses. A questionnaire included in the QA Plan (Appendix F in Papp et al., 1989) was used to guide this evaluation as well as to document each laboratory's performance in a consistent manner. The lead auditor summarized all observations in an audit report (see Appendix H) and brought any discrepancies to the attention of the laboratory manager.

Second-round technical systems audits were conducted in November 1988, after each laboratory had received two batches of soil samples and had completed analysis of the majority of parameters. By this time, preliminary data had been received by the QA staff via the modem-linked computer data entry system. The audit allowed an opportunity to discuss all problems associated with the data and the analytical methods. Of major concern to all laboratories during this audit were the new extraction procedures for CEC and subsequent cation analyses. The method specified that a polyester pre-plug and an Acrodisc™ be used in the extraction device rather than the cellulose filter pulp used in the earlier DDRP surveys. The laboratory managers suspected that the new procedures, which specified a larger quantity of soil, were not producing an efficient extraction because the mechanical extractor had a tendency to clog when extracting soils of high clay content. The procedures were subsequently modified to return to the use of cellulose filter pulp, but at a reduced quantity. During this audit, operation of the computer data entry and verification system (see Data Verification) was discussed and any questions pertaining to its use were answered. In general, the laboratories were functioning within the protocols of the contracts.

Third-round technical systems audits for Laboratories 1 and 2 were conducted in January 1989, while Laboratory 4 was visited again in March 1989. All preliminary data were reviewed, focusing on parameters not satisfying QE/QC criteria in a consistent manner. The sample reanalysis criteria and the procedures used by the QA staff to evaluate the data, including the DDRP measurement quality sample design, were discussed. The auditors toured each laboratory's facilities and held individual discussions with the laboratory technicians. The modified LEVIS data system used by Laboratory 2 for elemental analysis data was evaluated during the audit and problems were discussed and rectified.

Laboratories 1 and 2 underwent a fourth-round technical systems audit during May 1989. Laboratory 4 was not visited because the previous audits had shown this laboratory to be in control of all analysis and reporting tasks. Laboratory 1 had completed analysis on all of its batches, so this audit was conducted to review the final data, archive the computer hardware and analytical data base, discuss contractual issues, and specify procedures for returning the hardware and remaining soil samples to EMSL-LV. Laboratory 2 had been experiencing difficulty in satisfying the carbon ratio relationships for elemental analysis samples exhibiting low C_TOT concentrations; therefore, subsamples of the soils in Batch 30114 were sent to three other laboratories to verify the values reported by this laboratory. It was concluded that the Laboratory 2 data were valid, but that the theoretical chemistry relationships may not have been valid for elemental analysis at these low concentrations (Schumacher and Shaffer, in review). An appropriate delimiter was applied to each carbon relationship. This laboratory was also experiencing difficulty in satisfying the accuracy criteria in the extractable iron and aluminum analyses. The median-range audit samples for the latter batches in the survey showed a trend toward high bias and were outside the control limits when plotted on the QC charts. The problem appeared to be associated with higher than usual temperatures in the laboratory during the extraction phase of the analysis, which was conducted in an enclosed room with minimal ventilation. Once this situation was rectified, the samples were reanalyzed and the resulting data were of acceptable quality.

Special Studies

Before the MASS was implemented, the DDRP data users and QA staff raised some questions regarding soil preparation and analytical procedures. As a result, a series of small-scale research projects were undertaken to address the issues that were raised. Descriptions of the studies and their findings are provided in the following subsections.

Elemental Analysis Study

It was noted early in the MASS sample analysis that a relatively high number of carbon to nitrogen (C:N) and carbon to sulfur (C:S) ratios failed to satisfy the expected acceptance criteria for the total elemental analysis performed by Laboratory 2, especially for those samples having low C_TOT concentrations. The boundary conditions for the ratios were based upon theoretical and reported values for these ratios in the soil science literature. The C:N and C:S ratios were expected to be from 7 to 50 and 40 to 400, respectively, with delimiters applied to accomodate instrument variability at low concentrations. A study was conducted to determine whether: (1) the data generated by the laboratory were of acceptable quality, (2) bias was present in the data submitted by the laboratory, (3) the expected ranges established for the C:N and C:S ratios accurately represented the actual soil data, and (4) there was a particular source of error causing certain soil samples to exceed the acceptance ranges.

In the study, two independent laboratories and Laboratories 2 and 4 analyzed aliquots of the samples associated with Batch 30114 and reported the results in a specially coded Batch 39114. Laboratory 4 analyzed the samples using the MASS elemental analysis methods, while the independent laboratories and Laboratory 2 employed other commonly used methods for total elemental analysis. The results showed that a failure of six or more chemistry relationships in the batch occurred at all four laboratories using the established criteria. It was noted that most of the relationships failed on soils containing C_TOT of less than 0.3 percent. An evaluation of intralaboratory precision showed that the replication of C_TOT and N_TOT data was excellent, with only one observation above the acceptable variability limit. The S_TOT values were reproducible among the analytical laboratories, although not to the same degree as C_TOT and N_TOT (Schumacher and Shaffer, in review).

The study concluded that the data generated by Laboratory 2 for elemental analysis were of acceptable quality to justify their incorporation into the final MASS data base. The cause for the failure of the ratios appeared to be based within the empirical relationships and not in the data generated by the laboratory. It was determined that the relationships were originally developed for agricultural soils that were generally higher in total carbon, nitrogen, and sulfur than forest soils in the Mid-Appalachian region. Appropriate delimiters were used for applying the C:N and C:S ratios to low concentration samples.

Homogenization Study

In the previous DDRP surveys, a statistical logarithmic transformation of soil analytical data suggested that the soil sample homogenization procedure was possibly contributing an inordinate measure of uncertainty to the data. An extensive literature search revealed a lack of research specifically focusing on the precision and accuracy of various homogenization methods. Therefore, a study was conducted at EMSL-LV in the summer of 1988 to examine the various homogenization techniques used to prepare soil samples for analysis. Three of the most commonly used homogenization techniques were examined further: (1) cone-and-quartering, (2) riffle splitting using both open- and closed-bin riffle splitters, and (3) random sampling after disaggregating and sieving. A method evaluation was initiated using four soils of widely varying textures. Several subsampling approaches were used to evaluate the homogenization techniques, including the collection of subsamples after a series of passes during homogenization and a timed experiment to determine the efficiency of each technique. The analyses chosen to determine the effectiveness of each technique and the loss of fines from the system were particle size distribution, organic matter by loss on ignition, and pH in 0.01M calcium chloride.

The study concluded that use of either the closed- or open-bin riffle splitter is preferable to the cone-and-quartering or random sampling homogenization techniques. Cone-and-quartering required as much as six times longer for homogenization than riffle splitting and exhibited a greater loss of fines. Random sampling was the most time-effecient technique but was the least effective from a variability standpoint. The closed-bin riffle splitter is recommended over the open-bin riffle splitter due to its greater ability to retain the fines that could be lost as dust during homogenization. It was determined that five passes through the splitter are optimal to provide the most homogeneous sample, i.e., lowest variability, in terms of particle size distribution and organic matter, and additional passes apparently resulted in greater particle segregation (Schumacher et al., in review; Papp and Van

Remortel, in press). It was also determined by EMSL-LV statisticians that other statistical techniques, e.g., step function, applied to the data did not indicate the same type of inordinate homogenization uncertainty as the logarithmic transformation technique.

Filter Pulp Study

A study was initiated to examine the precision and physical advantages of several types of filter material utilized in the mechanical extraction of base cations from soils as specified in the MASS analytical methods (Blume et al., in press). An evaluation of alternatives to the continued use of Schleicher & Schuell™ No. 289 cellulose filter pulp was warranted because of cation contamination and its effect on CEC data observed in the previous surveys. Also, there were difficulties in using the standardized method for prewashing the pulp prior to use.

Three bulk fiber materials (cellulose pulp, polyester fiber, and rayon fiber) used for filtration, three types of disposable filter cassettes (teflon, nylon, and polysulfone), and five kinds of disposable membranes (two mixed esters, glass, polypropylene, and teflon) with reuseable holders were evaluated as alternatives to the cellulose pulp. The filter materials were evaluated for their physical suitability, contamination by six major soil elements, and the time required in extraction and equipment preparation between analyses.

The results of the study showed that the cellulose pulp was the most hydrophilic and possessed better packing qualities than either the polyester or rayon fibers. Chemical contamination was highest using the rayon fiber, especially for exchangeable sodium. However, each type of material exhibited distinct contamination characteristics for the six primary cations measured in the DDRP. The disposable membranes allowed soil to exude around the edges, and rupturing of the membranes occurred under vacuum. The nylon and polysulfone cassettes were much more reliable than the teflon cassettes which exhibited hydrophobic properties. In general, the cassettes were costly and difficult to set up, and accounted for some soil loss.

The study concluded that a polyester fiber plug placed in the syringe tip, used in conjunction with a cassette, greatly improved the extraction process and reduced soil loss and clogging of the filters. This apparatus was initially adopted for the MASS extractions. During the survey, however, it was determined that the apparatus was not suitable for soils high in clay due to ongoing clogging problems. As the cellulose fiber was easily available, inexpensive, easy to prepare, and demonstated reproducible extractions without soil loss, it was recommended that the use of cellulose filter pulp be continued for the MASS soil extraction methods. To minimize the potential for contamination, the size of the filter plug was reduced from 1.0 g to 0.5 g.

Independent Analysis of Calcium and Magnesium

During the survey, Laboratory 1 experienced difficulty in the analysis of calcium and magnesium (CA_OAC, CA_CL, MG_OAC, MG_CL, and MG_CL2) in Batch 30104 and magnesium (MG_CL2) in Batch 30125. Although two reanalyses of the batches were performed by this laboratory, the data continued to fail the acceptance criteria. Therefore, the two batches of samples were retrieved from Laboratory 1 and were recoded as Batches 39104 and 39125, respectively. Laboratory 4 was contracted to analyze the relabeled samples for the five parameters, with the anticipation that better data quality could be achieved for the two batches. The resulting data were of acceptable quality; therefore, the QA staff substituted these data in the analytical data base as replacements for the previous calcium and magnesium data from Laboratory 1.

Assessment Procedures

The QA staff at EMSL-LV was responsible for evaluating the results of the MASS sample analyses and reporting to the DDRP technical director on the quality of the verified data bases. The characteristics of data quality and their methods of assessment are described in the following subsections.

Quality Attributes

The attributes of data quality are qualitative and quantitative characteristics that are designed to provide an overall assessment of quality during the measurement phases of the MASS data collection activities. Measurement quality was defined in terms of the following six quality attributes:

- Detectability -- the determination of the low-range critical value of a soil characteristic that a method-specific procedure can reliably discern,
- Precision -- the level of agreement among multiple measurements of the same soil characteristic,
- Accuracy -- the level of agreement between an observed value and the "true" value of a soil characteristic,
- Representativeness -- the degree to which the soil data collected accurately represent the population of interest,
- Completeness -- the quantity of soil data that is successfully collected with respect to the amount intended in the experimental design, and
- Comparability -- the similarity of soil data from different sources included in a given set of data, and the similarity of methodologies from related projects across the regions of interest.

Measurement Quality Objectives

To address the overall DDRP objectives, conclusions must be based on scientifically sound interpretations of the data base. Accordingly, the EPA requires all monitoring and measurement programs to have established objectives for data quality based on the anticipated end uses of the data (Stanley and Verner, 1985; USEPA, 1986). The utility of the data is defined by the ability to confirm, reject, or discriminate among hypotheses formulated in the various DDRP computer simulation models. The primary purpose of the QA program is to increase the likelihood that the resulting data base meets or exceeds overall data quality objectives (DQOs). The quality of data can be quantified in relation to the DQOs, thereby allowing the data user to evaluate the hypotheses with a known level of confidence.

The methodology for establishment of DQOs has evolved over the course of the DDRP soil surveys. In contemporary usage, DQOs are statements of the levels of uncertainty that data users are willing to accept in the data. Uncertainty that exceeds the DQOs is considered to render the data unreliable in the judgement of the data users. The DQOs encompass all components of uncertainty resulting from sample measurement, operational activities, e.g., soil mapping or sample aggregation into sampling class/horizon configurations, and regional uncertainties, e.g., spatial variability. For the MASS QA program, measurement quality objectives (MQOs) were identified as a component of user-defined DQOs. The MQOs are specific goals defined by the data users that clearly describe the data quality that is sought for each of the measurement phases. They are defined quantitatively, where possible, according to quality attributes for each phase and are comparable to the "DQOs" specified in previous DDRP surveys.

The MQOs for the soil characterization, preparation, and analysis phases were specified in the MASS QA Plan (Papp et al., 1989). The survey objectives were reviewed by scientists familiar with analytical methods and soil characterization techniques, including soil chemists and laboratory personnel outside of the program. The MQOs were defined using information gained from the DDRP NE and SBRP surveys and from peer review comments in accordance with the analytical methods, instruments, and procedures selected.

Soil sampling in the MASS included the physical removal of soil samples from an excavated pit as well as the characterization of the soil pedon and sampling site (Kern and Lee, in press). The primary goal of the MASS sampling was to collect soil samples from representative pedons of 15 established sampling classes (Lee et al., 1989). The sampling classes were intended to represent the range of soil types encountered in the Mid-Appalachian region. The MQOs developed for sample analysis were not applicable to the field sampling activities, hence, specific sampling objectives were developed to ensure that field operations were conducted in a consistent manner and that an estimate of variability among sampling crews could be provided. The field sampling effort produced both qualitative and quantitative soil data from pedon characterization, e.g., soil color and horizon thickness, and quantitative data from soil analysis, e.g., field measured pH.

To assess the analytical MQOs, a series of measurement quality samples were analyzed together with the routine samples in a manner that was statistically relevant and which would allow conclusions to be drawn concerning the data quality. There are a number of assumptions and considerations upon which the batch sample design was based:

- The analytical MQOs could be attained if each batch satisfied the batch acceptance criteria set for the quality attributes.
- A two-tiered approach for measuring analytical precision would allow accurate assessment of the low concentration samples apart from the median and high concentration samples.
- Approximately 25 percent of the overall soil analysis effort would be applied to the analysis of measurement quality samples required for assessment purposes. There were approximately 40 samples in a batch, hence, about 10 of these were measurement quality samples.
- Measurement uncertainty at any given phase, e.g., analytical within-batch precision, could be evaluated with data from a minimum of 20 measurement quality samples of a given type (Barth et al., 1989). Since 27 mineral soil batches were analyzed during the MASS, a sufficient number of samples were present to make reliable across-batch statistical estimates.
- The primary sources of measurement uncertainty to be identified, controlled, and assessed were produced by sampling, preparation, and analysis activities.
- Each of the primary sources of uncertainty could be considered to be a combination of several smaller sources of uncertainty, e.g., the analytical component could include within-laboratory, within-batch, between-laboratory, and between-batch uncertainties.
- Accuracy includes the characteristics of bias in relation to predetermined audit sample accuracy windows, and laboratory differences and trends in relation to an accepted reference value within each window.

Details regarding the implementation and assessment of the analytical laboratory MQOs in the MASS are described in the following subsections. [NOTE: Some small changes to the QA program were implemented subsequent to the final submission of the MASS QA Plan (Papp et al., 1989). These included raising the required detection limit for AC_BACL from 0.25 to 1.25 meq/100g in organic soils. Also, an error was made in Appendix C of the QA Plan with regard to the soil:solution ratios used in the sample analyses. Table 1-1 of this report shows the actual ratios that were used by the analytical laboratories.]

Detectability

An important factor to consider in the measurement quality evaluation is the detection limit, which is defined as the lowest value of a characteristic that a method-specific procedure can reliably discern. The primary consideration in the evaluation of detectability is whether a measured sample value can be considered significantly different from the measured value of a sample blank (Keith et al., 1983). The probability that an analytical signal is not simply a random fluctuation is dependent on how many standard deviations the analytical signal varies from the mean value of blank responses (Long and Winefordner, 1983). The assessment of detectability issues in the MASS required an investigation of previously obtained precision data for low concentration samples.

A commonly recognized value for the detection limit is three times the standard deviation of a set of blank samples. A signal measured at this level or greater would have less than a 1-in-100 chance of being the result of a random fluctuation of the blank, assuming a one-tailed normal distribution of the blank samples. In the absence of "soil blank" samples, laboratory stock solutions and low concentration replicate samples have previously been used in the DDRP to estimate the variability expected of blank samples (Van Remortel et al., 1988; Byers et al., 1989). Although liquid blank samples were used extensively in the AERP aquatics surveys, development of a suitable synthetic soil blank for system-wide use in the DDRP has not been feasible.

With these limitations in mind, the DDRP data users and QA staff defined contract-required detection limits (CRDLs) based on the variability expected from a series of five calibration blanks analyzed in each batch of samples. The CRDLs were used in assessing contractual compliance by the analytical laboratories with regard to instrument detectability. Each laboratory was required to satisfy the CRDLs for specified parameters, as presented in Table 2-2. It was not appropriate to establish CRDLs for the particle size, pH, or sulfate isotherm parameters due to the nature of their measurement procedure, i.e., by gravimetric analysis, potentiometric readout, and sulfur solution, respectively; each of these parameters had expected ranges of concentration that were well above the critical detection limits of the relevant measuring devices.

The actual instrument detection limits (IDLs) measured throughout the survey by the laboratories were calculated from the pooled variability data of the calibration blanks. The IDLs identified the lowest analyte concentrations, averaged across batches, that could be reliably detected by the laboratories using the specified analytical instruments and procedures. During the actual sample analysis, IDLs were defined as three times the pooled standard deviation of at least 15 nonconsecutive calibration blanks run on three separate days. The IDLs were required to have values less than or equal to the CRDL. In some analyses a blank signal was not obtained; in these cases, the IDL was defined as three times the pooled standard deviation of 15 nonconsecutive replicate analyses of a standard whose concentration was four times the actual detection limit or the CRDL, whichever concentration was less. Acceptable initial IDLs were established prior to any sample analysis and subsequent IDLs were determined and reported on a batch-by-batch basis upon submission. Initial IDLs were valid for one month after their establishment; if more than one month had elapsed since establishment, the laboratories were required to establish new IDLs.

Table 2-2. Contract-Required Detection Limits for the Analytical Laboratories

Parameter	Reporting units	CRDL[a]	
		Units	mg/L
CA_CL	meq/100g	0.003	0.05
MG_CL	"	0.005	0.05
K_CL	"	0.002	0.05
NA_CL	"	0.003	0.05
AL_CL	"	0.015	0.10
CA_OAC	meq/100g	0.003	0.05
MG_OAC	"	0.005	0.05
K_OAC	"	0.002	0.05
NA_OAC	"	0.003	0.05
CEC_CL	meq/100g	0.15[b]	0.0075[b]
"	"	0.075[c]	1.05[c]
CEC_OAC	"	0.15[b]	0.0075[b]
"	"	0.075[c]	1.05[c]
AC_BACL	"	0.25[d]	0.005[d]
"	"	1.25[d]	0.025[d]
CA_CL2	meq/100g	0.0050	0.50
MG_CL2	"	0.0008	0.05
K_CL2	"	0.0003	0.05
NA_CL2	"	0.0004	0.05
FE_CL2	"	0.0005	0.10
AL_CL2	"	0.0011	0.10
FE_PYP	wt %	0.005	0.50
AL_PYP	"	0.005	0.50
FE_AO	"	0.005	0.50
AL_AO	"	0.005	0.50
SI_AO	"	0.005	0.50
FE_CD	"	0.002	0.50
AL_CD	"	0.002	0.50
SO4_H2O	mg S/kg	0.50	0.025
SO4_PO4	"	0.50	0.025
SO4_0	mg S/L	0.025	0.025
C_TOT	wt %	0.010	—
N_TOT	"	0.005	—
S_TOT	"	0.001	—

[a] Contract-required detection limit in reporting units and instrument units (mg/L or ppm), respectively.

[b] For titration method, in meq/100g and meq, respectively.

[c] For flow injection analysis (FIA) method, in meq/100g and meq/L, respectively.

[d] For mineral samples and organic samples, in meq/100g and meq, respectively.

NOTE: Detection limits not applicable for the physical parameters, soil pH, and the SO4_2-32 parameters.

The IDL determination for AC_BACL followed the same method used in the establishment of the initial IDL throughout the survey due to the strong dependence of the calibration blank upon the individual batch of extracting solution. For all other parameters, after the validity of the initial IDLs were established, the first batch of samples was analyzed and the IDLs reported for this batch were determined as composites of the calibration blanks from the batch and the calibration blanks run on the second and third day of the initial IDL determination. Similarly, the IDLs for other batches were established as composites of the calibration blanks from the batch being analyzed and the calibration blanks from the two previous batches or initial days, such that the calibration blanks were determined over three separate days and expressed as an "ongoing" IDL. It was essential that the analytical laboratories analyze the batches sequentially to establish the proper IDL determinations. If a given batch IDL was invalid, the batch was reanalyzed for that parameter.

At the end of the survey, independent IDLs (IIDLs) were calculated by the QA staff using the pooled variability data of the low concentration DL-QCCS samples across all batches. The IIDLs served as independent checks on the reliability of the IDLs because it was assumed that the variabilities associated with the calibration blanks and DL-QCCS samples would be similar.

Laboratory analysis, of course, is only one of many steps in the overall process of generating raw data for a soil sample collected from the field. For the MASS, it was possible to route low concentration audit samples through the field sampling phase and all subsequent phases of the measurement system, thereby allowing a system detection limit (SDL) to be estimated. The SDLs were calculated as three times the pooled standard deviation of the low-range field audit (FAL) samples from all mineral soil batches (see Measurement Quality Samples). Variability in the FAL samples encompassed uncertainty introduced during sampling, preparation, extraction, and analysis, and could include sample contamination incurred during any or all of these phases. This type of detection limit allowed a data user to identify when a given soil sample had a measured concentration that could be considered as statistically different from a reagent blank or calibration blank that had passed through the measurement system. For the MASS, the FAL samples exhibit many of the features that might be expected in a hypothetical soil blank sample; therefore, the resulting variability would be expected to parallel that of system-wide blanks.

Another important factor to consider in the evaluation of detectability is the implication of the calculated detection limits for assessing the quality of the routine data set. By estimating the percentage of routine sample data values that were greater than their corresponding SDLs, specific parameters were identified that might not have been measured precisely enough to satisfy the requirements of data users. Use of the SDL information in this manner is very similar to the establishment of a "decision limit" that is of value to the data modeling staffs. A high percentage of samples greater than the SDL was not necessarily the result of inadequate CRDLs, for it is possible that the instrumental error was not the primary source of variability affecting the FAL samples used to estimate the SDL for each parameter.

Precision

Precision is the level of agreement among multiple measurements of the same soil characteristic or parameter. A primary feature of the precision objectives is the two-tiered system for characterizing the MQOs and assessing the resulting data, as shown in Figure 2-2. The tiers were separated by a calculated "knot" value, established by dividing the precision objective for the lower tier by the precision objective for the upper tier and multiplying by 100. Intralaboratory within-batch precision objectives were defined for each of the two tiers. The lower tier concentration range below the knot defines the region of the data where the acceptable imprecision limits are absolute and expressed as a standard deviation in reporting units. The upper tier concentration range above the knot defines the region of the data where the acceptable imprecision limits are variable with concentration and expressed as a relative standard deviation in percent. This approach avoids setting restrictive precision objectives for low concentration soil samples which generally are more difficult to completely extract and analyze with a high degree of precision.

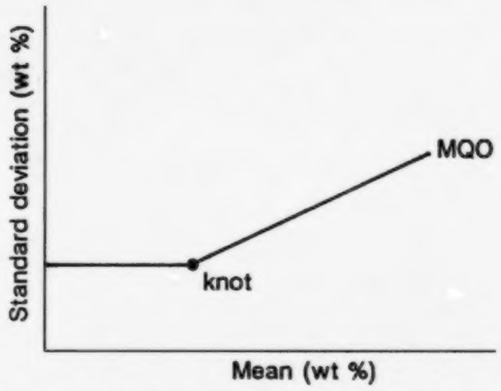


Figure 2-2. Example of two-tiered precision objective.

The two-tiered evaluation technique is characterized by a change in the slope of the activity line at the knot. The coordinates of the Y-axis expressed as an absolute standard deviation and the X-axis expressed as a mean value accurately show the percent RSD pictorially above the knot. This direct relationship is a unique characteristic of the plots, which include data from both mineral and organic soil samples. Due to wide ranges in concentration between the two types of samples, some plots were modified using scale breaks in order to incorporate both mineral and organic soil data. The scale breaks resulted in a corresponding change in the slope of the activity line.

The precision MQOs for the MASS were established for analytical laboratory within-batch precision of mineral soils and organic soils. Precision objectives were further defined for three types of measurement quality samples in accordance with their expected cumulative uncertainty. Field, preparation, and analytical measurement quality samples were used for this purpose. The precision objectives for the analytical samples are presented in Table 2-3. The precision objectives for the preparation samples were derived by multiplying the lower tier values in the table by 1 and the upper tier values by 1.5. The precision objectives for the field samples were derived by multiplying the lower tier values by 2 and the upper tier values by 3. These factors originated through interaction between the EMSL-LV and ERL-C staffs because it was known that subjecting a soil sample to increasing sources of measurement error usually results in higher uncertainty.

Two-tiered precision objectives were not required for the SAND, SILT, and CLAY parameters in the physical parameter group and for the PH_H2O, PH_002M, and PH_01M parameters in the pH parameter group. Instead, a single-tier objective was established as a standard deviation for the total concentration range of each of these parameters.

Table 2-3. Within-Batch Precision Objectives for the Analytical Measurement Quality Samples

Parameter	Reporting units	Mineral[a]			Organic[a]		
		SD	%RSD	Knot	SD	%RSD	Knot
MOIST	wt %	0.3	2.5	12.0	0.3	2.5	12.0
SAND[b]	"	3.0	—	—	—	—	—
SILT[b]	"	3.0	—	—	—	—	—
CLAY[b]	"	2.0	—	—	—	—	—
PH_H2O	pH units	0.10	—	—	0.10	—	—
PH_002M	"	0.10	—	—	0.10	—	—
PH_01M	"	0.10	—	—	0.10	—	—
CA_CL	meq/100g	0.02	10	0.20	0.10	10	1.0
MG_CL	"	0.02	10	0.20	0.10	10	1.0
K_CL	"	0.02	10	0.20	0.10	10	1.0
NA_CL	"	0.02	10	0.20	0.10	10	1.0
AL_CL	"	0.20	15	1.3	0.50	15	3.3
CA_OAC	meq/100g	0.02	10	0.20	0.10	10	1.0
MG_OAC	"	0.02	10	0.20	0.10	10	1.0
K_OAC	"	0.02	10	0.20	0.10	10	1.0
NA_OAC	"	0.02	10	0.20	0.10	10	1.0
CEC_CL	meq/100g	0.25	10	2.5	0.25	10	2.5
CEC_OAC	"	0.25	10	2.5	0.25	10	2.5
AC_BACL	"	1.0	15	6.7	1.0	15	6.7
CA_CL2	meq/100g	0.05	5	1.0	0.20	5	4.0
MG_CL2	"	0.005	10	0.05	0.05	10	0.50
K_CL2	"	0.005	10	0.05	0.025	10	0.25
NA_CL2	"	0.005	10	0.05	0.025	10	0.25
FE_CL2	"	0.01	15	0.07	0.05	15	0.33
AL_CL2	"	0.05	15	0.33	0.20	15	1.3
FE_PYP	wt %	0.03	10	0.30	0.03	10	0.30
AL_PYP	"	0.03	10	0.30	0.03	10	0.30
FE_AO	"	0.03	10	0.30	0.03	10	0.30
AL_AO	"	0.03	10	0.30	0.03	10	0.30
SI_AO	"	0.03	10	0.30	0.03	10	0.30
FE_CD	"	0.03	10	0.30	0.03	10	0.30
AL_CD	"	0.03	10	0.30	0.03	10	0.30
SO4_H2O	mg S/kg	1.5	10	15.0	1.5	10	15.0
SO4_PO4	"	1.5	10	15.0	1.5	10	15.0
SO4_0-32[b]	mg S/L	0.10	5	2.0	—	—	—
C_TOT	wt %	0.05	10	0.50	0.05	10	0.50
N_TOT	"	0.015	10	0.15	0.015	10	0.15
S_TOT	"	0.002	10	0.02	0.002	10	0.02

[a] Within-batch precision by standard deviation below the knot and by percent relative standard deviation above the knot for mineral and organic samples, respectively.

[b] Particle size and sulfate isotherm parameters were not analyzed for organic samples.

NOTE: For the preparation samples, lower tier objective is same as value in table, upper tier objective is 1.5x value; for the field samples, lower tier objective is 2x value, upper tier objective is 3x value (Papp et al., 1989).

The within-batch precision component measures the reproducibility of measurement quality sample data for a given batch of soil samples analyzed by one laboratory. Data from the laboratory audit samples were used to assess the analytical within-batch precision MQOs because the samples were not exposed to sampling error and were assumed to have negligible preparation error. The analytical between-batch precision component measures the reproducibility of laboratory audit sample data for different batches of soil samples analyzed by one laboratory on different days or at different times on any one day. The within-batch variability is usually expected to be somewhat smaller than the between-batch variability, although there were no specific MQOs defined for between-batch precision.

Previous DDRP surveys have shown that the error variance for many parameters is a function of analyte concentration (Van Remortel et al., 1988; Byers et al., 1989). It was discovered that no simple functional relationship could be established except that the error variance changes with concentration. For this reason, it was necessary to express the error variance by a step function where each step value represents an error variance for a specific interval of concentration (see Appendix J). The entire concentration range is divided into several intervals in such a way that the error variance within each interval is approximately independent of the analyte concentration, i.e., the error variance within each interval does not markedly change with analyte concentration (Miah et al., 1988). For example, if $F_1 \ . \ . \ F_k$ are multiple intervals on which the step function takes values $\sigma_1^2 \ . \ . \ \sigma_k^2$, then the error variance can be expressed as:

$$\sigma^2 = \Sigma_{\{i=1,k\}} \chi_i \sigma_i^2$$

where: χ_i is an indicator variable for the ith interval that allows variance estimation across intervals, independent of the individual intervals; χ_i takes a value of 1 if the analyte concentration falls in the ith interval, and 0 otherwise.

The overall analytical within-batch precision, i.e., averaged across batches, was estimated using only mineral soil laboratory audit samples because there were insufficient degrees of freedom to make reliable estimates of precision for the organic soil batches. The step function was used for each parameter to calculate a pooled variance from the B and Bw horizon laboratory audit pairs of samples. For comparison purposes, it was advantageous to express the variance in terms of a standard deviation in parameter reporting units, hence, the square root of the pooled variance was computed to generate a pooled standard deviation, s_p, across the lower range of concentration below the knot. The pooled standard deviation was calculated using the degrees of freedom for weighting purposes according to the formula:

$$s_p = [\ \Sigma_{\{i=1,k\}} (df_i \cdot s_i^2) \div \Sigma_{\{i=1,k\}} df_i\ ]^{1/2}$$

where: df_i is the degrees of freedom for the ith interval, and
s_i^2 is the error variance for the ith interval.

The pooled RSD value was used to assess data in the upper range of concentration above the knot and was calculated in the same manner except that the pooled standard deviation was divided by the weighted mean and the quotient was multiplied by 100.

The between-batch analytical precision was derived by pooling the appropriate laboratory audit sample mean values within each interval of concentration identified by the step function. The intervals were primarily defined by the distribution of data for the field duplicates, with additional refinement from the laboratory audit samples and preparation duplicates (see Appendix J). The resulting variability around the pooled mean of each interval was weighted by the degrees of freedom and was subsequently pooled across all intervals to estimate the average between-batch precision observed during the survey. These estimates were compared with the within-batch precision estimates to determine the relative magnitude of the batch error as a treatment effect.

Accuracy

Accuracy is the level of agreement between an observed value and the "true" value of a characteristic or parameter. In this report, data from the laboratory audit samples are used to estimate analytical accuracy and data from the field audit samples are used to assess accuracy from a system-wide measurement perspective. Natural soils were used as audit samples because a procedure for preparing synthetic soils was not established. Although the true chemical composition and physical characteristics of the audit samples were not defined, acceptance criteria for accuracy were established for the MASS based on extensive prior analysis of the samples by multiple laboratories in the two previous DDRP surveys. The Bw and C horizon audit samples were common to all three soil surveys. Data for the B horizon audit sample, used only in the MASS, were established during a preliminary evaluation.

During the MASS, the audit samples were not assumed to have a single "correct" reference value for each parameter. Instead, each audit sample type was given a range of acceptable values for each parameter in the form of an accuracy window which was developed using the previous DDRP analytical data. Each accuracy window was initially defined by a confidence interval placed around a biweight estimation (Kadafar, 1982) of the mean value across the two surveys. Additional refinements to the intervals were made by the data users and QA staff using ANOVA techniques and exploratory data analysis. From a contractual compliance standpoint, any observation that occurred within an accuracy window, i.e., between the lower limit and upper limit, inclusive, was considered to be unbiased and acceptable. Any observation below the lower limit or above the upper limit of the window was considered inaccurate for compliance purposes, as shown in Figure 2-3.

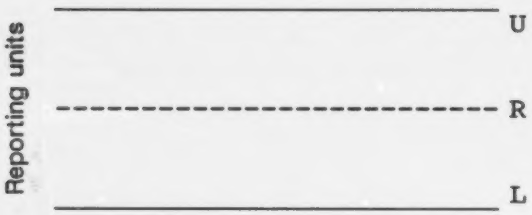


Figure 2-3. Example of an accuracy window with upper, lower, and reference values.

Accuracy was assessed by comparing the MASS analytical data to the accuracy window acceptance criteria defined for the different sample types. The aspects of accuracy investigated were bias, laboratory differences, and laboratory trends. Analytical bias was considered to be the quantitative measure of inaccuracy used in the evaluation of measurement uncertainty. Laboratory differences and trends served as quantitative and qualitative evaluations of analytical laboratory performance during the MASS.

During the MASS sample analysis, any audit sample values that fell within the limits of the accuracy windows were assumed to be unbiased with respect to the batch acceptance criteria. For data evaluation purposes, however, bias was estimated from the mean of the accuracy window, i.e., the reference value, for each parameter. In this framework, analytical bias for a specific audit sample was defined as follows:

$$B_j = \Sigma (Y_{jk} - R_j) \div n_j$$

where: B_j is the bias for the jth audit sample,
Y_{jk} is the average observed value for the jth audit sample and k observations,
R_j is the reference value $[(U_j + L_j) + 2]$ for the jth audit sample, and
n_j is the number of samples of the jth audit sample type used in the assessment.

Bias as a function of analyte concentration was also investigated and it was determined that the magnitude of the bias in relation to imprecision was very small. As a result, no empirical relationship between bias and imprecision was observed. It was deemed unnecessary from a practical viewpoint to investigate whether concentration dependency was a demonstrated characteristic of bias. Therefore, it was assumed that bias was independent of concentration for the purposes of this survey.

A calculated bias value for each parameter was compared to the corresponding SDL and, if the bias was less than the SDL, analytical bias was considered to be negligible. The weighted average bias for the laboratory audit samples was used as the bias estimate for each parameter, such that:

$$B_a = \Sigma_{\{j=1,J\}} (n_j \cdot B_j) + \Sigma n_j$$

where: B_a is the average weighted analytical bias for the ath parameter.

The relative effect of observations outside an accuracy window was evaluated with respect to the bias estimate. The relative magnitude of "outlier error" is assessed using the ratio of outside-window bias to the total bias estimate. The percentage of samples that were outside the window also provided a basis for identifying inordinate outlier effects.

The laboratory difference, d, is defined as the difference between the mean of a repeated measurement and the reference value, R_a, for a given parameter. The individual differences were pooled across audit samples to establish the performance of each analytical laboratory in relation to the reference value. The O horizon audit sample was omitted from the pooling because all organic samples were analyzed only by Laboratory 4. Hence, data for the B, Bw, and C horizon audit samples were pooled and weighted by the number of audit samples of each type for each laboratory. This quantity was divided by the reference value that had also been pooled and weighted across audit samples, and the quotient was multiplied by 100 to yield the average percent difference from the pooled reference value.

The analysis of variance (ANOVA) was used to determine significant differences among the audit sample data reported by the analytical laboratories. A two-way ANOVA model (Steel and Torrie, 1960) was used to test the significance of differences between laboratory means pooled across audit samples, based on a similar approach detailed in Schmoyer et al. (1989). A pair-wise comparison at the .05 level of significance was performed on the laboratory means using Scheffe's multiple comparisons test (Arnold, 1981). The results of this test were used to identify laboratory differences of significance and to define the ranking order for those differences.

The analytical laboratories were subsequently evaluated by determining the significance of their average deviation from the reference value. The prior distribution, μ, of the reference value for each parameter was assumed to be uniform within each accuracy window, and the variance, V, of the prior distribution was calculated as:

$$V_j(\mu) = (U_j - L_j)^2 \div 12$$

such that the value "12" is the lowest common denominator for the expected squared error of the prior reference distribution and the square of its mean. The squared deviation, S_L^2, from the corresponding reference value was estimated for each analytical laboratory as:

$$S_{Lj}^2 = \Sigma(Y_{jk} - R_j)^2 \div n_j$$

where: S_{Lj}^2 is the squared deviation for the Lth laboratory and the jth audit sample.

To allow the presentation of squared deviation estimates in parameter reporting units, the square root of each S_{Lj}^2 term was calculated and defined as the average deviation from the reference value.

The mean squared error, $\hat{E}_L(\epsilon^2)$, serves as the justification for comparison of the squared deviation and prior distribution variance terms and was estimated for each analytical laboratory as:

$$\hat{E}_{Lj}(\epsilon^2) = S_{Lj}^2 - V_j(\mu)$$

Using data pooled across audit samples, the squared deviation was assessed with respect to the variance of the prior distribution and expressed as a ratio (Box et al., 1978). The data from those laboratories showing a ratio of 3:1 or greater were identified as different in relation to the data from the other laboratories for a given parameter.

The laboratory audit sample data were also examined for trends which might be caused by instrumental drift or other problems that might have occurred at a particular laboratory over the course of the survey. For this purpose, three-point moving averages (Massart et al., 1988) of the audit sample data, grouped by laboratory, were plotted in a temporal sequence.

Representativeness

The evaluation of representativeness included: (1) determining whether the routine samples collected were representative of the sampling class characteristics, (2) assessing the sample homogenization and subsampling procedures by measuring the ability of the preparation laboratory to prepare representative subsamples from the bulk soil samples collected by the sampling crews, and (3) assessing the ability of the field duplicate samples to adequately represent the range and frequency distribution of analyte concentrations in the routine samples. This latter consideration is important when assessing the effects of concentration dependency on the calculation of measurement uncertainty.

Soil types identified in the Mid-Appalachian region were combined into sampling classes that were expected to have similar physical and chemical characteristics. Each of the sampling classes could be sampled across a number of watersheds in which they occurred. In this approach, a given soil sample did not necessarily represent the specific watershed from which it was collected; rather, it contributed to a set of samples which collectively represented a specific sampling class for all watersheds within the sampling region. The sampling crew leader selected a sampling site representing the designated sampling class and vegetation class within the designated watershed according to the sampling protocols (Appendix A in Kern and Lee, in press). Both the qualitative and quantitative data collected were intended to be representative of soils in the region.

During the survey, homogenization of the samples at the preparation laboratory in conjunction with subsequent homogenization at the analytical laboratory were specified to ensure that a uniform and representative source of sample was available from which to select aliquots for analysis. Precision data from the preparation duplicates were used to assess the representativeness of samples created by the preparation laboratory homogenization and subsampling procedures, while data from the laboratory audit samples and analytical duplicate samples were used to assess representativeness of the aliquots used for analysis.

The Kolmogorov-Smirnov two-sample test, i.e., the KS-statistic, was used to estimate the maximum distance between the cumulative distributions of two data sets (Conover, 1980). Data sets of the routine samples (RS) and the field duplicates (FD) were tested to determine whether the distributions were similar. The significant KS-statistics, i.e., significant at the .05 level, were defined according to the critical value, V_c , for the FD/RS comparison. The critical value is based on a sample size n_1 and n_2 for the data sets being compared, where:

$$V_c = 1.36 [(n_1 + n_2) \div (n_1 \cdot n_2)]^{1/2}$$

The algorithm yielded a critical value for FD/RS of 0.185. If the KS-statistic exceeded the critical value for a particular pairing, the FD data set was considered to be possibly nonrepresentative of the distribution of routine samples. It was assumed that representativeness of the preparation duplicates (PD) data set in relation to the RS data set would mimic the FD/RS comparison because the preparation duplicates were subsampled directly from the field duplicates and their associated routine samples. Therefore, the KS-statistic was not applied to the PD data set.

Completeness

Soil sampling protocols in the MASS specified the sampling of 100 percent of the designated pedons and their component horizons to a depth of two meters, with the exception of certain undecomposed organic horizons, intermittent horizons, horizons less than three centimeters thick, and horizons containing dense fragipan material or a prohibitive amount of stones and boulders (Kern et al., 1988). The soil preparation protocols specified that each batch of samples sent to an analytical laboratory should include the proper array of measurement quality samples. The preparation laboratory was required to complete the specified analyses and processing tasks for 100 percent of the samples that satisfied the sample receipt verification criteria. Each batch of samples sent to a contracted analytical laboratory was required to contain a specified configuration of routine samples and measurement quality samples.

The analytical completeness objective specified the analysis of 90 percent or more of the parameters for all samples analyzed (Papp et al., 1989). It was possible to attain 100 percent completeness if a sufficient quantity of each sample was available to complete all analyses and subsequent requested reanalyses. Analytical completeness was evaluated using routine data from the MASS verified and validated data bases.

Comparability

Comparability of data from the three DDRP surveys was determined to be a complex issue with several levels of detail which should be considered, such that:

- Level 1 data comparability is established on the basis of statistical evaluation methods, measurement quality samples, and the field sampling, preparation, and analytical methods used.
- Level 2 data comparability is established by the acceptability and useability of the verified data bases as defined by the data users.
- Level 3 data comparability allows the direct quantitative comparison of data for each parameter of interest.

Comparability assessment begins, therefore, with the Level 1 data comparisons. If the statistical techniques and uncertainty terms are comparable across surveys, the different types of measurement quality samples used in the surveys are compared. If identical types of samples were used, the field sampling, sample preparation, and sample analysis methods are compared. If the methods used in the surveys were different, the data are not directly comparable. If identical methods were used, Level 2 criteria are applied to identify the least restrictive precision/accuracy quality objectives and estimates associated with the different data bases. It is assumed that the least restrictive criteria defines the acceptability of all data used in the comparison. In addition, a confirmation of the useability of data generated under the least restrictive criteria defines those data that are recommended for use by the community of data users. Therefore, data that satisfy the Levels 1 and 2 criteria can be quantitatively compared at Level 3. Data not satisfying the Level 2 criteria are highlighted for the data user by outlining the comparability restrictions of the data. Ultimately, the data user decides which comparisons can be made and which user criteria are appropriate for a given data analysis. An experimental Level 3 assessment, using the data without regard to Levels 1 and 2 criteria, can be performed to confirm or reject the hypothesis that highlighted data at the first two levels are not directly comparable.

The verified analytical data bases for the NE, SBRP, and MASS surveys were used for the comparability assessments described in Section 3. While it is recognized that accuracy is the preferred measure of data comparability, precision is sometimes the only attribute that can be compared. Accuracy is used in the comparability assessment wherever possible.

As an independent assessment of comparability, an interlaboratory comparability study was conducted to determine whether the analytical data for the natural soil audit samples analyzed by the contract analytical laboratories for the DDRP soil surveys are comparable to data for the same samples analyzed by other analytical laboratories in the United States and Canada. A summary of the findings of this study is provided in Section 3, and a detailed accounting of the study is contained in a separate report (Fenstermaker et al., in preparation).

Uncertainty Estimation

The term "uncertainty" describes the sum of all quantifiable errors associated with a particular portion of a measurement system or population of interest. Measurement uncertainty in the MASS data was controlled through clearly-defined protocols and technical systems audits, and by the introduction of measurement quality samples during each sample measurement phase. Each quantifiable component of the precision and accuracy attributes was identified individually for the three different measurement phases of the program (sampling, preparation, and analysis) and collectively for overall measurement uncertainty on a parameter-by-parameter basis. In addition, an estimate was made, using the routine sample data set, of the overall data uncertainty in the population of soil samples collected from the Mid-Appalachian region during this survey.

Statistical Model

Standard operating procedures and specified protocols were followed in each measurement phase of the MASS. Depending on its limitations or assumptions, each procedure induced a random error for each physical or chemical characteristic of a soil sample. The sum of these errors can be defined as the data collection error, which is treated as a random variable. This variable can be used in an additive model (Cochran, 1977) and serves as an estimate of uncertainty in a data set, such that:

$$y = \mu + \epsilon$$

where: y is an observed sample characteristic,
μ is the "true" sample characteristic, and
ϵ is the data collection error, which is assumed to be the sum of the errors generated by the independent measurement phases.

The identification of the error distribution throughout the measurement phases requires a large number of replicate measurements which, from a budgetary and logistical standpoint, can be restrictive. However, a relatively small number of observations can be used to estimate the first two moments, i.e., the mean and variance, of the data collection error. The moments are sufficient to estimate inaccuracy and imprecision of the routine data in an additive model. For this report, the standard deviation (SD) in reporting units and the relative standard deviation (RSD) in percent were used to assess the precision components. The analytical bias was considered to be the quantitative measure used to assess the accuracy component.

The sum in quadrature of the imprecision and inaccuracy error terms represents the measurement uncertainty in the different measurement quality sample data sets, and includes both measurement and population uncertainty in the routine sample data set. In order to make effective use of the MASS data, the evaluation of measurement uncertainty in relation to the overall data uncertainty is essential.

The expected squared error was used as an estimate of uncertainty and was calculated as the sum of the error variance and the square of the bias term described previously in this section and in Appendix J. The error terms can be defined only for a given analyte concentration range because the error variance changes with analyte concentration; however, the entire concentration range can be partitioned into intervals and a step function is applied to those intervals in such a way that each step value is the squared error, $\hat{E}_i(\epsilon^2)$, for a specific interval of the entire concentration range (Miah et al., 1988).

For most data interpretation uses, it is preferable to convert the squared uncertainty values into the standard reporting units of the parameters of interest. This conversion is made simply by calculating the square root of the squared error. To evaluate the data uncertainties associated with the routine data, the $\sqrt{\hat{E}_i(\epsilon^2)}$ terms from each interval were pooled and weighted by the proportion of routine sample concentrations within the corresponding intervals. The resulting uncertainty estimate, δ or delta, is defined as:

$$\delta = \Sigma P_i \sqrt{\hat{E}_i(\epsilon^2)} \div \Sigma P_i$$

where: δ is the pooled uncertainty for all intervals over the concentration range,

P_i is the proportion of routine samples in the ith interval, and

$\hat{E}_i(\epsilon^2)$ is the mean squared error for the ith interval, and represents the sum of the error variance and the square of the bias for the ith interval.

Occasionally, a dearth of measurement quality sample precision data within one or more intervals made it impossible to calculate a variance for that portion of the concentration range. In those cases, δ is a conditional estimate of uncertainty because the sum proportion of samples across all intervals represented is less than 1.0 and the resulting conditional uncertainty value usually is overestimated. In other situations, certain portions of the precision data were incomplete, e.g., for between-batch precision. In these cases, δ is considered to be a partial estimate because specific additive components are missing, and the resulting numerator variance term is underestimated. As a result of both possibilities, particular intervals were occasionally excluded from the uncertainty calculations for some parameters.

Sampling Class/Horizon Groups

The soil mapping units identified in the watersheds of the Mid-Appalachian region were too numerous to allow statistically-based sampling of all soil components. As an alternative, soils were grouped into sampling classes, shown in Table 2-4, that were believed to have similar physical and chemical properties in relation to soil responses to acidic deposition. Field sampling sites were randomly selected from the areas of occurrence of each sampling class because the objective of the sampling was to characterize sampling classes rather than individual watersheds or soil types. Prior to the MASS, the degree of heterogeneity of physical and chemical properties for individual sampling classes and soil horizon types was not known. The QA data analyses of the two previous DDRP surveys, however, have shown that measurement uncertainty in the routine samples is confounded with the sampling class/horizon heterogeneity in the calculated imprecision estimates. Because these two characteristics vary widely with respect to each other, the ratio of measurement uncertainty to overall sampling class/horizon variability is not constant but can be ascertained through a series of data set comparisons.

In estimating the relative importance of measurement uncertainty, mean values and

Table 2-4. Sampling Classes Used to Group Different Soil Types

Sampling class	Soil types
CMS	Entisols: mine spoils
CFP	Entisols: somewhat poorly drained and wetter
FLW	Entisols: moderately well drained and drier Inceptisols, Spodosols: no fragipan, flooded
HST	Histosols: all
BNS	Inceptisols, Spodosols: no fragipan, not flooded, shallow
BMK	Inceptisols, Spodosols: no fragipan, not flooded, moderately deep, skeletal
BMD	Inceptisols, Spodosols: no fragipan, not flooded, moderately deep, non-skeletal
BND	Inceptisols, Spodosols: no fragipan, not flooded, deep
BXW	Inceptisols: Ochrepts
BXP	Inceptisols: Aquepts
TWM	Ultisols, Alfisols: no fragipan, moderately well drained and drier, moderately deep
TWD	Ultisols, Alfisols: no fragipan, moderately well drained and drier, deep
TPD	Ultisols, Alfisols: no fragipan, somewhat poorly drained and wetter
TXP	Ultisols, Alfisols: fragipan, somewhat poorly drained and wetter
TXW	Ultisols, Alfisols: no fragipan, moderately well drained and drier

Table 2-5. Primary Horizon Types for Sampling Class/Horizon Groups

Horizon type	Routine samples		Sampling classes represented[b]
	n[a]	%	
A	65	7.7	14
Ag	3	0.4	2
Ap	30	3.6	11
AE	9	1.1	6
Bhs	6	0.7	4
Bt	106	12.6	5
Btg	11	1.3	3
Btx	27	3.2	3
Bw	157	18.6	11
Bwg	11	1.3	3
Bx	47	5.6	4
Bxg	10	1.2	3
BA	38	4.5	11
BC	42	5.0	9
C	162	19.2	15
Cg	25	3.0	5
Cr	9	1.1	4
Cx	9	1.1	4
E	29	3.4	10
EB	7	0.8	5
Oa	19	2.3	7
Oe	22	2.6	9

[a] N = 799 (844 total routine samples minus 45 samples classified as "special interest" samples in the verified data base.

[b] There are 148 sampling class/horizon groups.

variances for the sampling class/horizon groups were determined for each soil parameter and quantitatively compared to the uncertainty estimate generated by the measurement system. There are as many as 22 primary horizon types associated with each of the 15 sampling classes, forming a total of 148 distinct sampling class/horizon groups. Table 2-5 presents the number and percentage of primary horizon types and the number of sampling classes associated with each horizon.

For this report, four delta values have been calculated: δ_1 , δ_2 , δ_3 , and δ_4 values. The uncertainty estimates are generally expected to increase with increasing sources of confounded error. The δ_4 values are calculated from the sampling class/horizon groups of routine samples, while the other three δ values are calculated using data from the measurement quality samples described below.

It has been proposed that a measured value can be considered as essentially errorless for most uses if the uncertainty in that value is one-third or less of the permissible tolerance for its use (Taylor, 1987). The QA staff examined the relation of measurement uncertainty to overall data uncertainty in the routine samples, where the overall measurement uncertainty was based on the δ_3 values calculated from the field duplicate samples (see Appendix C). The magnitude of this uncertainty in relation to the associated δ_4 data uncertainty values generated from the sampling class/horizon groups provides the data user with a basis for assessing the uncertainty contribution of the measurement system. For the purposes of this assessment, the data uncertainty confounded in the sampling class/horizon groups is considered to be a surrogate for user-defined error tolerance values. Where δ_3 is one-third or less of δ_4, measurement uncertainty is a negligible contribution to the overall data uncertainty.

Measurement Quality Samples

The design of the MASS QA program incorporated the concept of batch sample analysis where analytical samples were combined into batches, each containing approximately 40 samples, at the preparation laboratory. Within these batches, a series of different types of measurement quality samples were randomly inserted and were used to evaluate and, in some cases, control various components of measurement uncertainty. There were two distinct groups of measurement quality samples used in the MASS design: quality evaluation (QE) samples and quality control (QC) samples. The QE samples allowed an independent assessment of measurement quality by the QA staff, while the QC samples enabled a laboratory to control measurement error and satisfy contractual requirements.

It was not feasible to provide one measurement quality sample whose entire variability is an estimate of overall measurement uncertainty. However, the combination of two or more different types of measurement quality samples that include all of the quantifiable components of measurement uncertainty provides a reasonable and defensible quality estimate. Figure 2-4 provides a flowchart of the QE and QC samples that were placed in each mineral or organic batch of analytical samples.

The configurations of the batches were representative of the array of sampling crews and the quantity of samples collected by each crew. The 27 mineral sample batches were distributed evenly among the three contract analytical laboratories for analysis. Also, the distribution of mineral soil samples was balanced with respect to the sampling crews and analytical laboratories, such that a nearly equal percentage of samples collected by one sampling crew were analyzed by each laboratory (see Table 2-6). The two organic batches were sent to Laboratory 4 because the laboratory demonstrated superior performance in analyzing organic soils during the PE sample analysis.

Quality Evaluation Samples

The QE samples are those measurement quality samples which were either blind or double-blind to the sampling crews, preparation laboratory, and analytical laboratories. By definition, a blind sample has a concentration range that is unknown to the analyst, whereas a double-blind sample cannot be distinguished from a routine sample and has a concentration range that is unknown to the analyst (Taylor, 1987). These samples provided an independent check on the QC process and were used to evaluate measurement quality for any given batch or across all batches. Important characteristics of the QE natural soil audit samples include their similarity to routine samples in matrix type and concentration level, homogeneity and stability, and defined accuracy windows. The QE duplicate samples were subsampled from specific routine samples. Every QE sample had a specific purpose in the data assessment scheme, as described below and in Table 2-7.

The number and percentage of QE and routine samples shipped to the analytical laboratories are shown in Table 2-8. A description of each QE sample is provided in the following subsections.

Field Duplicate (FD) Sample

For every third pedon sampled, a FD sample was collected from a horizon selected at random by the sampling crew leader in such a way that the range of possible soil horizon types encountered was sampled over the course of the survey. The sampling crew placed alternate trowels-full of soil into separate bags to produce a pair of samples (one routine, one duplicate) from one specific horizon within a specific pedon. The FDs were expected to contain the largest amount of confounded uncertainty of all measurement quality samples, as noted previously in Table 2-3. Data from the FDs were not specifically intended to control field sampling imprecision but were used to control imprecision at the preparation laboratory and analytical laboratories. Individual pairs were used primarily to estimate system within-batch imprecision, and were pooled to provide the within-batch component of the δ_3 overall measurement uncertainty, i.e., the confounded uncertainty associated with sampling, preparation, and analysis.

Table 2-6. Distribution of Field Measurement Quality Samples and Routine Samples Among the Sampling Crews and Analytical Laboratories

Sampling crew	Field measurement quality samples[a]																Routine samples[b]			
	L1					L2					L4					Percent by crew	L1	L2	L4	Percent by crew
	FD	C	B	Bw	O	FD	C	B	Bw	O	FD	C	B	Bw	O					
WV01	1	1	2	0	0	2	2	2	2	0	2	2	2	2	0	17.2	29	57	51	16.2
WV02	2	2	2	2	0	2	2	2	2	0	2	2	2	2	0	20.7	46	64	62	20.4
PA01	3	3	2	4	0	2	2	2	2	0	3	2	2	2	3	27.6	85	59	78	26.3
PA02	2	2	2	2	0	2	2	2	2	0	3	2	2	2	3	24.1	65	52	87	24.2
PA03	1	1	2	0	0	1	1	0	2	0	1	1	0	2	0	10.4	35	35	39	12.9
Percent by Lab					31.0					31.0					38.0	100.0	30.8	31.6	37.6	100.0

[a] The laboratory measurement quality samples were present in the batches in the same quantity as the field samples, except that the PDs are considered in place of the FDs (PD = 2 x FD). [Total = 116 (FD=29, C=27, B=26, Bw=28, O=6)].

[b] Number and percentage of routine soil samples, respectively. (Total = 844).

Table 2-7. Status and Assessment Purpose of the Measurement Quality Soil Samples

Sample type	Status of sample[a]				Assessment purpose[b]			
	QA staff	Sampling crew	Preparation laboratory	Analytical laboratory	System	Sampling	Preparation	Analysis
FD	B	B	B	DB	PW	PW,R	PW	PW
FAP/FAO	K	B	B	DB	PW,A	PW,A	PW,A	PW,A
FAL	K	B	B	DB	D,A	D,A	D,A	A
PD	B	–	B	DB	–	–	PW,R	PW
LAP/LAO	K	–	–	DB	–	–	–	PW,PB,A
LAL	K	–	–	DB	–	–	–	D,PB,A
AD	–	–	–	B	–	–	–	PW
QCAS	K	–	–	K	–	–	–	A

[a] K = known concentration, B = blind (unknown concentration), DB = double blind (unknown identity and concentration).

[b] D = detectability/contamination, PW = within-batch precision, PB = between-batch precision, A = accuracy, R = representativeness.

Table 2-8. Number and Percentage of Quality Evaluation and Routine Samples

Sample type	Mineral samples		Organic samples	
	n	percent[a]	n	percent[a]
FD	27	2.4	2	0.2
FAP/FAO	54	4.9	6	0.5
FAL	27	2.4	0	0.0
PD	54	4.9	4	0.4
LAP/LAO	54	4.9	6	0.5
LAL	27	2.4	0	0.0
Routine[b]	795	72.1	49	4.4

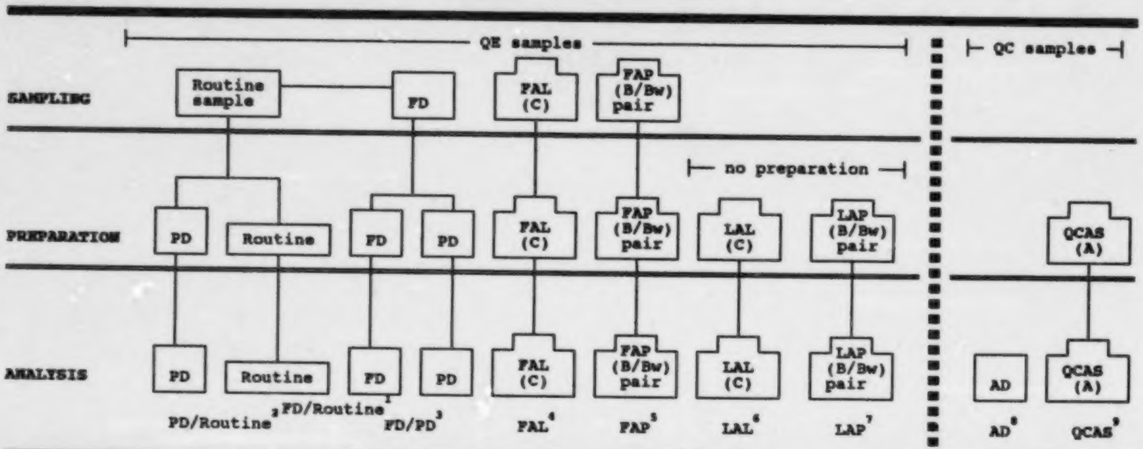
[a] Percentage based on N = 1,105 (total quality evaluation and routine samples).

[b] Does not include quality control, comparability, or special study samples

Field Audit (FAP or FAO) Sample

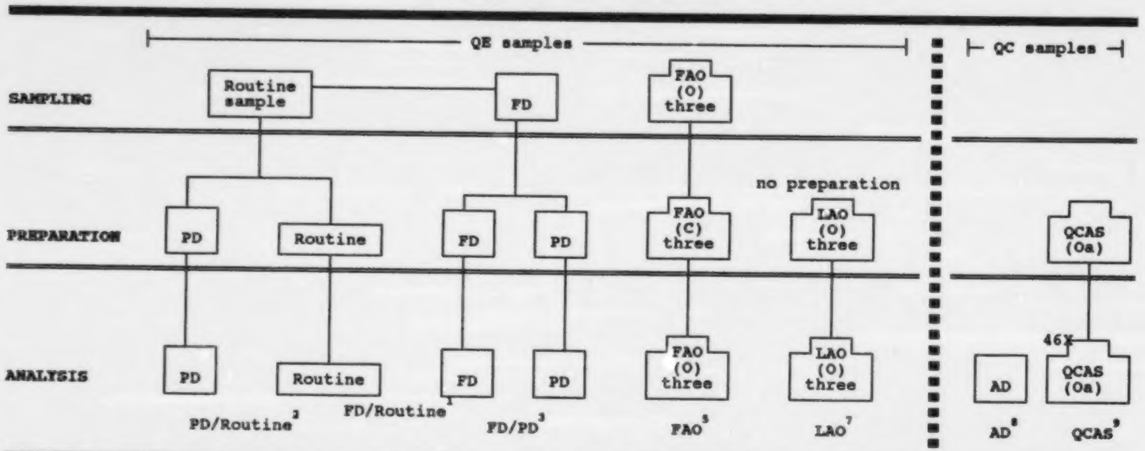
The FAP samples are median-range B or Bw horizon field audit samples that the QA staff sent in pairs to the sampling crews. The FAO samples are median-range O horizon field audit samples that the QA staff sent in triplicate to the sampling crews. The FAP and FAO samples were processed as if they had just been obtained from the excavated pit, i.e., the samples were sieved and bagged in the same manner as the routine samples at the same sampling sites where FD samples were collected. The field audit samples subsequently underwent the same soil preparation and analysis steps as the routine samples. The FAP and FAO samples were used in the analytical phase to estimate system precision and accuracy for mineral and organic batches,

MINERAL SOIL BATCHES



FD = field duplicate; FAL = low-range field audit; FAP = field audit pair; PD = preparation duplicate; LAL = low-range laboratory audit; LAP = laboratory audit pair; QCAS = quality control audit sample; AD = analytical duplicate.

ORGANIC SOIL BATCHES



FD = field duplicate; FAO = field audit triplicate (organic); PD = preparation duplicate; LAO = laboratory audit triplicate (organic); QCAS = quality control audit sample; AD = analytical duplicate.

[1] System within-batch precision.
[2] Within-batch precision.
[3] Within-batch precision.
[4] System detection limit.
[5] System accuracy and within-/between-batch precision.
[6] Analytical accuracy.
[7] Analytical accuracy and within-/between-batch precision.
[8] Within-batch precision.
[9] Analytical accuracy.

Figure 2-3. Quality evaluation and quality control soil samples for mineral and organic batches.

respectively. The B and Bw horizon FAP sample pairs were alternated between batches (see Table 2-6.

Low-Range Field Audit (FAL) Sample

The FAL sample is a low concentration C horizon field audit sample that the QA staff sent with each pair of FAP samples to the sampling crews. The FAL sample was handled in the same general manner as the FAP samples, and was used to identify contamination in the measurement system and served as an additional check on system-wide accuracy. Pooled FAL data from all mineral soil batches provided an estimate of the system detection limit (SDL), which was calculated as three times the pooled standard deviation of the FAL samples.

Preparation Duplicate (PD) Sample

A pair of PD samples, one split from the FD sample and one split from its associated routine sample, was created at the preparation laboratory immediately following sample homogenization and was placed in each batch. The PDs were used to identify the soil preparation uncertainty component of measurement uncertainty and as an independent check on within-batch precision of the analytical laboratories. These samples characterized the measurement uncertainty introduced during and after homogenization/subsampling at the preparation laboratory, but did not include uncertainty related to sample drying or sieving, or any contamination occurring prior to sample homogenization. The uncertainty attributed to sample preparation was derived after identifying and isolating the uncertainty from sample analysis. The preparation laboratory activities were monitored through the evaluation of PD precision in the initial sample batches. Precision data from the PD samples were later used by the QA staff to estimate the δ_2 confounded uncertainty associated with homogenization/subsampling at the preparation laboratory and with sample analysis at the analytical laboratories.

Laboratory Audit (LAP or LAO) Sample

The LAP samples are median-range B or Bw horizon laboratory audit samples, identical to the FAP samples, that the QA staff sent in pairs directly to the preparation laboratory for inclusion in each mineral soil batch sent to an analytical laboratory. The LAO samples are O horizon laboratory audit samples, identical to the FAO samples, that were sent in triplicate by the QA staff directly to the preparation laboratory for inclusion in each organic soil batch. The LAP and LAO samples were used to assess analytical within-batch precision and accuracy and were used in combination with the FAP and FAO samples to identify sources of contamination or method error. Comparison of the laboratory audit sample data across batches allowed the QA staff to identify interlaboratory differences and to assess the between-batch component of analytical precision. Pooled LAP and LAL data were used to estimate the δ_1 uncertainty associated with sample analysis.

Low-Range Laboratory Audit (LAL) Sample

The LAL sample is a low concentration C horizon laboratory audit sample, identical to the FAL, that the QA staff sent directly to the preparation laboratory for inclusion in each mineral batch sent to an analytical laboratory. The LAL samples were used primarily to assess analytical accuracy at low analyte concentrations. In addition, the LAL samples were evaluated in conjunction with the FAL samples to identify the source and magnitude of any suspected sample contamination.

Quality Control Samples

In order to produce data of consistently high quality, the contract laboratories were required to analyze certain types of QC samples that were known to the laboratory staff and that could be used by the analysts to identify and control both random and systematic measurement errors. The QC samples were non-blind samples procured under contract to assist the laboratories in satisfying the laboratory MQOs and included soil samples, e.g., analytical duplicates, and non-soil samples, e.g., reagent blanks. Some of the QC samples were created by the laboratories to evaluate instrument calibration and standardization and to identify problems such as contamination or analytical interference.

Each QC sample had certain specifications, as listed in Table 2-9, that were required to be satisfied before data for the parameter or batch were accepted. The QC samples

Table 2-9. Quality Control Requirements for the Analytical Sample Batches

Characteristic	Parameter	Requirement
QC Audit Sample (QCAS)	ALL	Within accuracy window
Analytical Duplicate (AD)	ALL	Satisfies precision limits
Calibration Blank		
number analyzed	ALL[a,b]	((samples in batch/10) + 1)
measured	ALL[a,d]	≤ CRDL
Reagent Blank (mean)	PH_H20, PH_002M, PH_01M	4.5 ≤ mean ≤ 7.5
	SO4_2 - 16	± 3% of theoretical
	SO4_32	± 2% of theoretical
	ALL OTHERS[d]	≤ CRDL
QC Check Sample (QCCS)		
number analyzed	ALL	((samples in batch/10) + 1)
measured	SO4_0 - 32	± 5% of theoretical
	ALL OTHERS[e]	± 10% of theoretical
Detection Limit QCCS (DL-QCCS)	ALL[e]	± 20% of theoretical
Matrix Spike Recovery	SO4_0 - 32	95% ≤ x ≤ 105%
	ALL OTHERS[e]	90% ≤ x ≤ 110%
Absorption Spike Solution	SO4_0	≤ CRDL
	SO4_2 - 16	± 3% theoretical value
	SO4_32	± 2% theoretical value
	CA_CL2	± 5% theoretical value
Ion Chromatography Resolution	SO4_H2O, SO4_PO4, SO4_0-32	Resolution ≥ 60%
Instrument Detection Limit (IDL)	ALL[a,c]	≤ CRDL
Sample Weight	ALL	Measured = ± 5% method
Sample Volume	ALL	Measured = method

[a] Except moisture, particle size, and pH parameters.
[b] Except SO4_2-32.
[c] Except AC_BACL.
[d] Except FSI, CLAY, and AC_BACL.
[e] Except moisture, particle size, AC_BACL, and SO4_0,4,16 parameters.

were analyzed by each laboratory and allowed the laboratory manager and the QA staff to assess whether the physical and chemical analyses were in control. The QC samples used in the MASS are detailed in the following subsections.

Quality Control Audit Sample (QCAS)

The QCAS is a median-range A or Oa horizon laboratory audit sample that the QA staff sent directly to the preparation laboratory for inclusion as the 15th sample in each mineral or organic batch, respectively. This sample had predetermined accuracy windows that were established from reference values and confidence intervals computed from previous DDRP analyses. The windows for each parameter were provided to the analytical laboratories and were programmed in the computer data entry system. The QCAS was used to control bias and to reduce between-laboratory and between-batch measurement uncertainty. Data for the QCAS were evaluated by a between-batch control chart to ensure that the results were within acceptable inaccuracy limits. If the QCAS did not satisfy the accuracy criteria, the affected batch of samples was re-extracted and reanalyzed for the parameter in question.

Analytical Duplicate (AD) Sample

A duplicate subsample of the 25th sample in each batch (triplicate for pH parameters) was selected as the AD sample at the analytical laboratory and was used by the laboratory manager to ensure that the analytical within-batch precision MQOs were satisfied. Acceptance criteria for the replicate analyses were based on concentrations, below the knot, being less than or equal to an absolute standard deviation, or less than or equal to the percent RSD above the knot. If data for an AD sample exceeded these criteria, the batch analysis was halted and the problem was investigated. Subsequently, additional samples were analyzed in duplicate or triplicate until the analytical system was brought under control. At this time, the entire batch of samples was reanalyzed for the parameter in question.

Calibration Blank Sample

The calibration blank was generally defined as a zero mg/L standard containing only the matrix of the calibration standards with no analyte present. The two exceptions to this definition were: (1) the calibration blank for CA_CL2 which was prepared in deionized distilled water instead of calcium chloride solution, and (2) the calibration blank for AC_BACL which had a concentration requiring 26.0 to 36.0 mL, i.e., 1.3 to 1.8 meq, of titer to neutralize the buffered base.

One calibration blank per batch was analyzed immediately after the initial instrument calibration to check for significant baseline drift. During batch-wide analysis, calibration blanks were run before the first sample, after every 10 samples, and after the last sample of the batch. The observed concentration of the blank was required to be less than or equal to the CRDL, except for AC_BACL. If the concentration was greater than the CRDL, the instrument was rezeroed and the calibration curve was rechecked. Any samples bracketing the "bad" calibration blank were reanalyzed. The within-batch data from the calibration blanks were used to calculate ongoing IDLs across batches.

Reagent Blank Sample

When an analytical method required sample preparation, e.g., for extraction, a reagent blank for each group of samples was prepared and analyzed. A reagent blank is a sample composed of all reagents in the same quantities used in preparing an actual sample for analysis. Reagent blanks underwent the same digestion or extraction procedures as an actual sample, in the absence of a soil matrix. The concentration of the reagent blank was required to be less than or equal to the CRDL for all except the particle size, pH, exchangeable acidity, extractable calcium, and sulfate isotherm (excluding zero mg S/L) parameters. No check was performed on the reagent blank for particle size analysis. All three pH parameters had reagent blanks with values between 4.5 and 7.5, inclusive. The AC_BACL and CA_CL2 reagent blanks were required to have concentrations between 1.3 and 1.8 meq and 76 and 84 mg/L, respectively. The sulfate adsorption isotherm analysis used reagent blanks that were within ± 3% of the theoretical concentration for the SO4_2-16 parameters and within ± 2% of the theoretical concentration for the SO4_32 parameter. If a reagent blank concentration exceeded the allowable limits, the source of error was identified and eliminated. A new reagent blank was prepared and the affected batch of samples was re-extracted and reanalyzed for that parameter.

Quality Control Check Sample (QCCS)

Immediately after an instrument calibration, a QCCS containing the analyte of interest at a known concentration in the mid-calibration range was analyzed. The QCCS was analyzed to verify the calibration curve prior to any sample analysis, after every 10 samples, and after the last sample of a batch. The QCCS solution was required to be selected from a stock solution different than that used in the preparation of standards for the instrument calibration. The QCCS data were plotted at each laboratory on a QC chart which showed if the QCCS analysis exceeded the established limits, which were defined as a ± percentage interval for each batch and as 95- and 99-percent confidence intervals (warning and control limits, respectively) for the between-batch results. If a QCCS value exceeded a ± 10 percent interval around the theoretical concentration (± 5 percent for the sulfate isotherms) or was outside the control limits on the QC chart, the QCCS was considered to be unacceptable. The instrument was recalibrated and all samples subsequent to the last acceptable QCCS were reanalyzed.

Detection Limit Quality Control Check Sample (DL-QCCS)

The DL-QCCS is a low-range QC sample that contained the analyte of interest at a specified concentration, usually two to three times the CRDL. The purpose of the DL-QCCS was to eliminate the necessity of formally determining the detection limit on a daily basis. The sample was run once per batch and the measured value was required to be within 20 percent of the theoretical concentration. If this criterion was not satisfied, the source of error was identified and corrected, and all samples in the batch were reanalyzed before routine sample analysis was resumed.

Matrix Spike Sample

A matrix spike is a QC sample used to determine possible chemical interferences that might affect an analytical result. For liquid samples, e.g., cation extractions, one matrix spike sample was prepared for each batch and each parameter by spiking an aliquot of a solution with a known quantity of analyte prior to analysis. The spike concentration was approximately equal to the endogenous level or 10 times the detection limit, whichever was larger. The volume of the added spike was negligible, i.e., less than or equal to one percent of the sample aliquot volume.

For solid samples, e.g., aliquots for C_TOT, one matrix spike sample was prepared for each batch and each parameter by adding a known weight of material containing the analyte of interest to a sample of known weight. The spike concentration was twice the endogenous level or 10 times the detection limit, whichever was larger. The concentration of the matrix spike was not allowed to exceed the linear range of the instrument. Although it was not negligible, the weight of the spike material was considered negligible for calculation purposes.

Matrix spike recoveries were required to be between 95 and 105 percent, inclusive, for the sulfate isotherms and between 90 and 110 percent, inclusive, for all other spiked parameters. If the spike recovery was not acceptable, two additional, different samples in the batch were spiked with the analyte of interest. If the recoveries of the two additional spiked samples failed to satisfy the criteria, the entire batch of samples was required to be reanalyzed for that parameter by the method of standard additions. All matrix spike data for the MASS satisfied the criteria and the method of standard additions was never implemented.

Adsorption Spike Solution

The adsorption spike solutions were: (1) the extraction solution used in determining CA_CL2, or (2) the extraction solution standards used for generation of the SO4_0-32 parameters. For each batch of samples, the adsorption spike solutions were analyzed in triplicate. Measured concentrations for the solution were 76 to 84 mg/L Ca^{2+} for the 0.002M calcium chloride extraction. Spike solutions for the sulfate isotherms had values less than or equal to the CRDL for SO4_0, ± 3% of the theoretical concentration for SO4_2-16, and ± 2% of the theoretical concentration for SO4_32. If any adsorption spike solution did not satisfy these criteria, a new batch of extraction solution was prepared and any samples that were equilibrated using the "bad" solution were re-extracted and reanalyzed.

Ion Chromatography Resolution Sample

An ion chromatography resolution test was performed once per analytical run by analyzing a standard that contained concentrations of approximately 1 mg/L each of sulfate, phosphate, and nitrate. The analysis was run to ensure "clean" separation of eluant peaks for the individual ions measured, which is necessary for proper quantification of sulfate. The resolution between the sulfate peak and either the phosphate or nitrate peaks was required to be greater than 60 percent as calculated by the following formula:

$$2(a + b) \times 100$$

where: a is the distance between peaks, in centimeters, and
b is the width of the peak base, in centimeters.

If the resolution did not exceed 60 percent, the column was replaced and the resolution test was repeated until satisfactory resolution was obtained.

Data Verification

Different types of errors in the MASS analytical data base were identified through the data verification activities and were subsequently confirmed or corrected. These included:

- data entry errors, i.e., values from the analytical laboratory data packages that were entered incorrectly;
- transcription errors, i.e., data that were transposed or transcribed incorrectly at the analytical laboratories;
- batch errors, i.e., systematic or sporadic errors that were discovered when most or all of the data in specific batches were outlying; and

- laboratory errors, i.e., systematic or sporadic errors that were discovered when some or all of the data in batches from a specific laboratory were outlying.

Details of the data verification procedures are provided in the following subsections.

Design and Implementation of LEVIS

A computerized Laboratory Entry and Verification Information System (LEVIS) was developed for implementation on personal computers and was utilized during the MASS analytical data collection activities. The LEVIS program is a two-phase menu-driven system, in which phase one is an analytical laboratory data entry and control system and phase two is an external quality assessment system.

The conceptual design and detailed specifications for LEVIS were prepared at EMSL-LV in collaboration with MASS participants from ERL-C and ORNL. The design incorporated MASS data management concerns that could affect the LEVIS operation, ranging from project management issues to the selection of computer hardware and software. The DDRP management team selected the support staff at ORNL to perform the computer programming of phase one and EMSL-LV to develop phase two. Personnel from both groups worked together to produce the final design and to maintain a common understanding of the design characteristics. Periodic reviews of the phase one programming implementation were performed to ensure the correct adaptation of the conceptual design and project operations. The data base manager at EMSL-LV served as the primary point of contact for LEVIS problems discovered by the laboratories.

Compatibility with IBM-AT™ computer hardware was essential to the selection of appropriate personal computer systems. Specifications included a 40-megabyte hard drive, 1.2-megabyte floppy disk drive, keyboard, color monitor, printer, and 2400-baud modem. A computer system containing all of these components was installed at each analytical laboratory. A similar system with a larger capacity hard disk served as the central computer at EMSL-LV. The central computer received and maintained data from all three laboratories.

Phase one included a data entry component and two laboratory components of the verification system: the QC summary reports and the soil chemistry relationships (SCRs). A single entry of data at the laboratories, with 100 percent visual verification of the entries, was required. The LEVIS program generated hard copy printouts of the input data files which were checked against the laboratory raw data sheets by the data entry personnel. The LEVIS program performed the calculation of final values, i.e., instrument readings adjusted to the soil sample, corrected for moisture content and converted to parameter reporting units.

Phase one was programmed in dBase III Plus™ and then compiled. Communications software was installed that would facilitate the transfer of data files from the laboratories to the central computer at EMSL-LV. This utility also allowed the central computer to operate as a remote terminal to the laboratory computer when the two were connected via modem, and commands typed on the central computer were executed on the laboratory computer. This allowed the QA staff to review laboratory data files, run programs, select data files for transfer, and remotely transfer data to and from the central computer. Archive utility software was also used to copy and compress the entire data base for a batch into one file suitable for transfer. Through this utility, a data file size reduction of 80 percent was common. As the time required for a file transfer is directly related to the size of file, the use of an archive utility reduced the time required for data transfer from one hour to less than fifteen minutes per batch. The backup of the laboratory data bases to floppy disks also used the software to reduce the required backup storage capacity.

Data management personnel from EMSL-LV and ORNL attended a meeting following the completion of phase one programming to review the system. Minor changes were identified and completed before the system was installed in a personal computer supplied by the EPA to each of the three analytical laboratories. Members of both staffs installed the equipment and trained the laboratory personnel. Installation included the hardware and software set-up as well as additional system testing. Training included a project overview and the use of LEVIS hardware and software, analytical methods, QE/QC sample design and evaluation, data collection forms, and a thorough review of all LEVIS components and operations. Analytical laboratory personnel who participated in the training usually included the laboratory manager, analysts, and data entry operators. To facilitate the training, a LEVIS user's guide was produced (SAIC, 1988) and a "test batch" was installed on each system.

The programming of phase two did not begin until phase one was completed and installed. The data base design and structure created in phase one was different from the data base structure required for phase two or for the final MASS data base structure. The phase one programming documentation was used in creating conversion programs to accomodate data from both phases.

Phase two incorporated two additional verification programs to evaluate QE samples for precision and accuracy. Both programs were implemented on the central EMSL-LV personal computer. This procedure converted the phase one data base files to the phase two data base structure before evaluation programs were run. Phase two was programmed in PC-SAS™ Version 6.03, which had been selected for structuring all of the completed DDRP data bases. Although PC-SAS™ is not a compiled programming language, the use of the applications facility module allowed the entire system to be menu driven so that the operators never interacted directly with the programming code.

Analytical laboratories were occasionally required to reanalyze a batch of samples because of some identified or suspected QE or QC discrepancy. The LEVIS program was designed to accommodate the entry of up to ten reanalyses of each parameter and maintain all versions in the active data base. The analytical laboratory was required to identify the analytical run selected for submission to the QA staff. This was accomplished with a submission selection option and a submission tracking file.

Verification Checks

The analytical laboratories evaluated batch data as part of the laboratory QC procedures, and the QA staff evaluated preliminary batch data transmitted via modem from the analytical laboratories. The preliminary data were usually incomplete because of later amendments or supplements by the analytical laboratories, although evaluation of these data was extremely useful in the early diagnosis of potential problems which might otherwise have been justification for reanalysis requests. Early identification of problems allowed the laboratories to begin corrective steps prior to completing analysis of all parameters in a given batch. Data evaluation of the formal submission package ensured that the data were of acceptable quality and that the hard-copy data package submission was identical to the corresponding data submitted on floppy disk. The formal submission data were used in constructing the MASS final verified data base.

Verification checks were implemented in both phases and included QC summary reports, soil chemistry relationships (SCRs), and evaluations of precision and accuracy. The data evaluation process in phase one incorporated the summary reports and SCRs, which were available to both the analytical laboratory and QA staff. The phase two programming, which incorporated the precision and accuracy evaluations, was not accessible by the analytical laboratories and was processed only by the QA staff.

Quality Control Summary Report

The QC summary report consisted of a 10-page report that listed various data quality checks for the analytical parameters and a summary page that allowed a quick overview of the QC requirements for any potential deficiencies. The ALSOW mandated that these requirements be satisfied before a batch of data could be accepted for payment. The QC summary report checked the following batch data characteristics:

- number of samples analyzed in each run and a flag indicating the run number selected for submission;
- mean values and ranges of variability for each parameter;
- replicate sample evaluation;
- percent matrix spike recoveries;
- calibration blank, reagent blank, QCCS, and DL-QCCS results;
- QCAS accuracy results;
- weights and volumes used;
- spike solution concentrations; and
- instrument detection limits.

The reported data were checked by LEVIS to ensure that the laboratory had fulfilled its contractual requirements. Data failing to satisfy the requirements were automatically appended with verification flags (see Appendix A). Confirmation or reanalysis of any flagged parameters was requested if a flag appeared on any pages of the summary report.

Soil Chemistry Relationships (SCRs)

Sixteen SCRs were checked by LEVIS during the data verification. The SCRs were viewed as established empirical relationships for soil systems and were expected to fail in fewer than 10 percent of the samples. Appropriate delimiter constraints were built into each of the SCRs to account for either instrument imprecision or an exceptions to the theories upon which the relationships were based, as presented in Table 2-10 below.

Relationships involving particle size analysis and sulfate isotherm data were not applied to organic soils because these parameters were not required analyses. From a contractual standpoint, the failure of six or more relationships in a batch for any SCR constituted a major flag requiring reanalysis of the batch, and one to five failures constituted a minor flag that allowed for the possibility of reanalysis if other acceptance criteria were not satisfied.

The SCRs were especially useful in identifying data entry errors and providing information about possible anomalies within a given pedon. Data transcription errors were more easily identified due to the random failure of one or more samples to fulfill a particular relationship. In some cases for which a parameter was used in multiple relationships, such as SO4_H2O, it was possible to identify which parameter data file contained the transposed or questionable values. The results for a given sample might find one relationship failing and the other passing, thereby indicating a problem with the other parameter in the relationship.

A potential discrepancy was also indicated if the same sample numbers failed several relationships. In one batch, for example, seven samples were flagged for failing both the pH and CEC relationships, and five of the samples failed both relationships. Investigation of the field data forms for these seven samples revealed that the five samples were collected from the same pedon, suggesting that the failures were not related to the laboratory analysis but to some anomaly occurring within that pedon.

Precision Evaluation

With the exception of the phase one precision estimates for the AD samples and any internal analyses conducted by the laboratories, the analysis of laboratory precision was performed only by the QA staff who evaluated data for the FAP/FAO, LAP/LAO, FD, and PD measurement quality samples. The samples were evaluated for precision using either an absolute standard deviation or a percent RSD depending upon the mean value in relation to the knot, as described previously. Different levels of imprecision were established to account for the varying degrees or types of error that were expected in the measurement quality samples. Less precision was expected, for example, between the FAP samples than between the LAP samples due to the possibility of the FAP samples containing field sampling or preparation error. The LEVIS program flagged the data for a given parameter if the precision of the replicate samples did not satisfy the established precision criteria. Data reported for each pair or triplicate of samples included the mean, standard deviation, percent RSD, and an identifier code revealing which of the criteria was used in evaluating the data for each parameter.

Accuracy Evaluation

With the exception of the phase one accuracy estimates for the QCAS samples, the analysis of laboratory accuracy was performed only by the QA staff using the accuracy windows defined for the MASS laboratory audit samples. The windows were used to check the accuracy of the individual LAL samples and of the mean of the LAP samples for each parameter. Data values were flagged if the results were not within the accuracy window. Data were also evaluated for the FAP, FAL, and individual LAP samples, although these results were not used as a basis for requesting reanalysis from the analytical laboratories. Each accuracy printout listed the sample data value, the accuracy window range, and the absolute plus or minus difference of the sample value from the acceptable limits of the window.

Summary pages of the QE and QC accuracy data were generated for all audit samples in a batch. Summary pages included the number of samples outside the accuracy

Table 2-10. Soil Chemistry Relationships and Delimiters

Soil chemistry relationship	Delimiter
PH_H20 > PH_002M > PH_01M	if pH differences were > 0.05 units
CA_CL + MG_CL + K_CL + NA_CL < CEC_CL	if CEC_CL > 1 meq/100g and pH_H2O < 7
AL_CL < 0.01 meq/100g	if PH_H20 > 6.0
CA_OAC + MG_OAC + K_OAC + NA_OAC < CEC_OAC	if CEC_CL > 1 meq/100g and pH_H2O < 7
CEC_OAC > CEC_CL	if CEC_CL > 1 meq/100g and PH_H2O < 7
CEC_OAC + CLAY < 50	if CLAY > 1.0 and CEC_CL > 1 meq/100g
CEC_CL + CLAY < 50	if CLAY > 1.0 and CEC_CL > 1 meq/100g
MG_CL2 < MG_CL * 1.10	if MG_CL2 > 0.008 meq/100g
K_CL2 < K_CL * 1.10	if K_CL2 > 0.003 meq/100g
NA_CL2 < NA_CL * 1.10	if NA_CL2 > 0.03 meq/100g
4 < SO4_H2O + SO4_0 < 20	if SO4_H2O ≥ 2 mg S/kg and SO4_0 ≥ 0.1 mg S/kg
SO4_PO4 > SO4_H20[a]	if SO4_PO4 > 1 mg S/kg
SO4_32 > SO4_16 > SO4_8 > SO4_4 > SO4_2 > SO4_0	if SO4_32N ≤ 7.5 mg S/kg
SO4_32N > SO4_16N > SO4_8N > SO4_4N > SO4_2N > SO4_0N[b]	if SO4_32N ≥ 7.5 mg S/kg
7 < C_TOT + N_TOT < 50	if C_TOT ≥ 0.1% and N_TOT ≥ 0.03%
40 < C_TOT + S_TOT < 400	if C_TOT ≥ 0.1% and S_TOT ≥ 0.005%

[a] SO4_PO4 was multiplied by 1.10 for organic soils
[b] N = mean spike concentration of initial solution — (instrument reading × dilution factor)

windows, the absolute plus or minus difference from the limits of the windows, and the mean, maximum, and minimum values of the absolute differences for the batch. The summary pages were used to determine whether an outlier was sample-specific or was consistent throughout all audit sample horizon types and were helpful in showing where analytical difficulties might have been occurring at an analytical laboratory.

Confirmation and Reanalysis Requests

Following the completion of the initial data evaluation process for a batch, the QA staff prepared a summary document of all flagged parameters, indicating whether a flag originated from an unacceptable value for the QC, SCR, precision, or accuracy criteria. The number and severity of the flags for each parameter were checked using a QA reanalysis template (QART) to determine if reanalysis was required. The templates were constructed in the manner of a spreadsheet, where rows specify the evaluation criteria and columns give the criteria which determine the severity of measurement uncertainty that had occurred for each parameter (see Appendix B).

Two levels of magnitude were defined on each QART, namely, major or minor flags. A major flag occurred if any two of the following four evaluations of the laboratory audit samples and preparation duplicates were unacceptable: (1) precision of the PD/routine pair, (2) precision of the PD/FD pair, 3) precision of the LAP samples or accuracy of their mean value, or 4) accuracy of the LAL sample. A major flag was also applied if six or more of the same SCRs failed in the batch. A major flag resulted in batch confirmation and/or reanalysis for that parameter. Minor flags were applied if only one of the four evaluations of the laboratory audit samples or preparation duplicates failed, if the FD or FAP precision was unacceptable, or if a SCR failed in one to five instances. Three or more minor flags were comparable to a major flag for a given parameter. Reanalysis was not requested if fewer than three minor flags occurred for any parameter in a batch. If a major flag or three minor flags were not identified by the QART for any parameter, then a sample batch was deemed to be of acceptable quality. After confirmation, the data were formally accepted and transferred into the preliminary verified data base, and the analytical laboratory was authorized to receive payment for the analyses.

Data confirmation was performed independently of the LEVIS program. Where a data entry error was identified, the analytical laboratory was requested to re-enter the correct data in the computer and submit to the QA staff a new floppy disk and any appropriate LEVIS data forms in which the suspect value or data correction for the parameter was checked. This phase of data confirmation did not influence the formal acceptance of the batch data.

The QA staff compiled verification reports for each batch data submission. A letter describing potential discrepancies within the reported data was sent to each laboratory after evaluation of the data package. Occasionally, the letter and an accompanying DDRP Form 500 (see Appendix K) suggested where errors may have occurred, e.g., transposed numbers or erroneous dilution factors. The laboratories were required to respond promptly with confirmation or reanalysis of the parameters in question. If reanalysis was necessary, the analysis was performed on the entire batch of samples for the parameters of interest rather than on individual samples in the batch.

Internal Consistency Checks

After completion and receipt of all final batch data from the analytical laboratories, two different internal consistency checks were performed to check for possible data outliers. Most of the verification checks and evaluations described previously were performed on data from the QE and QC samples, and it was believed that additional evaluations beyond the SCRs would be useful in identifying suspect values in the routine soil sample data. The purpose of these evaluations was to identify, for each analytical parameter, outlying values that were not consistent with the majority of values observed. Confirmation requests of any suspected outliers identified by these checks were made to the analytical laboratories, and the raw data used to generate these values were subsequently checked for errors in transcription, data entry, calculation, or editing. Fewer than 10 percent of the suspected outliers were changed as a result of this confirmation process.

If no correction was made as result of the checks, each outlying value was flagged in the analytical data base (see Appendix A). It was not possible for the QA staff to identify or verify the cause of every individual outlier with the laboratories, although confirmation of each value was requested. A provision was made in the QART which allowed a major reanalysis flag to be placed on a batch of data if more than 10 outliers were identified. However, it never became necessary to apply this provision to an analytical laboratory during the MASS.

Statistical Outlier Check

For the first internal consistency check, a computer program was used to develop a correlation matrix for all analytical parameters measured in the MASS. The strongest correlations, based on the coefficient of determination (r^2), were investigated in more detail (see Table 2-11). In many cases, the values for one parameter did not correlate well with values for any other parameter. Correlations were not performed on parameters within the same extract or from the same measurement, e.g., CA_OAC values were not correlated with MG_OAC values even though the resulting r^2 value might have shown the strongest correlation. The reason for this decision was that certain errors, e.g., incomplete extraction, would not be identified by examining correlations within the same extracting solution.

Table 2-11. Internal Consistency Checks Performed for Parameter Correlations

Parameter Correlations[a]		r^2 value
SAND	MS	0.58
SAND	FSI	0.80
VCOS	COS	0.46
VFS	FS	0.24
SILT	COSI	0.43
SILT	FSI	0.84
CLAY	SAND	0.59
PH_H2O	PH_01M	0.88
PH_01M	PH_002M	0.94
CA_CL	CA_OAC	0.99
MG_CL	MG_OAC	0.99
K_CL	K_OAC	0.97
NA_CL	NA_OAC	0.80
CEC_CL	CEC_OAC	0.76
AC_BACL	AL_CL	0.61
AC_BACL	CEC_OAC	0.74
MG_CL2	MG_CL	0.70
K_CL2	K_OAC	0.82
AL_CL2	SO4_PO4	0.35
FE_PYP	FE_AO	0.60
AL_PYP	AL_AO	0.73
FE_CD	CLAY	0.59
AL_CD	AL_AO	0.72
SO4_PO4	SO4_H20	0.75
SO4_0	SO4_H2O	0.99
SO4_2	SO4_H2O	0.91
SO4_4	SO4_H2O	0.91
SO4_8	SO4_H2O	0.93
SO4_16	SO4_H2O	0.84
SO4_32	SO4_H2O	0.72
C_TOT	N_TOT	0.68
S_TOT	SO4_4	0.88

[a] A variable may appear in more than one correlation, and not all variables were used in the correlations.

Application of a Cook's D statistic (Belsley et al., 1980) was useful in determining high influence points. This statistic is a version of the difference of fit statistic applied in the internal consistency checks of previous DDRP surveys, and serves to measure the change resulting from the deletion of each point from the routine data set (Van Remortel et al., 1988). Essentially, the Cook's D statistic is used to scale and square the difference of fit statistic to allow extreme values to stand out more clearly (SAS, 1986).

A list of outlying values was developed through a multi-stage regression process for those parameter correlations exhibiting the highest r^2 values. For each parameter pair, a regression line was fit to the data and a set of outlying values and leverage points was generated which included those points having a Cook's D residual of 1.0 or higher. These points were temporarily removed from the data set and the regression was re-run. At this stage, each point was individually placed into the second regression; if the outlier had a new residual value of 3.0 or higher, then it was positively identified as an outlier. Finally, the axes of the parameters in the regression were reversed and the procedure was repeated, yielding another set of outliers. The two sets, not mutually exclusive, constituted the final outlier points that were checked by the QA staff and underwent confirmation at the analytical laboratories.

A list of outlying values was sent on a DDRP Form 600A (see Appendix K) to each analytical laboratory with instructions that these values be confirmed or corrected by the laboratory manager. Any outliers that were not changed to "acceptable" values as defined by the regression were appended with an "X4" flag (see Appendix A) in the analytical data base. Approximately 3 percent of the data underwent confirmation as a result of this consistency check.

Pedon/Horizon Outlier Check

For the second internal consistency check, the analytical data were listed in a data set using the original soil profile sequence, i.e., pedon and horizon, of the samples. Data for each pedon were visually scanned by soil scientists for consistency in the magnitude of the parameter values from one horizon to the next. This check allowed for subjective identification of data which appeared to be distinctly aberrant in relation to its horizon type or to the adjacent horizons within the pedon.

Where individual values appeared to be very inconsistent with the surrounding horizon data in a pedon, a list of outlying values were sent on a DDRP Form 600B (see Appendix K) to each analytical laboratory for confirmation or correction by the laboratory manager. Any outliers that were not changed to "acceptable" values as defined by the horizon configuration were appended with an "X5" flag (see Appendix A) in the analytical data base. Approximately 2 percent of the data underwent confirmation as a result of this consistency check.

Overview of the Data Bases

The field sampling and sample preparation data were entered into separate SAS-AF™ raw data files on personal computers at EMSL-LV. The analytical data were entered into LEVIS on personal computers located at the laboratories. All raw data forms were archived by the laboratories for possible future reference use. The field data were verified according to the criteria specified in Appendix G of the MASS QA Plan (Papp et al., 1989). The preparation data were verified according to the criteria specified in Appendix H of the QA Plan. The analytical data were verified according to the criteria specified in the ALSOW (USEPA, 1988). Raw data verification was accomplished by a systematic evaluation of completeness, precision, internal consistency, and coding accuracy. Apparent discrepancies were appended with data qualifiers, or flags, unless they could be corrected. After verification was completed on July 14, 1989, the data bases were "frozen" and did not undergo further editing by the QA staff.

Verified data from the analyses conducted during sample preparation were later appended to the verified analytical data base. The "frozen" verified field and analytical data bases were then sent to ORNL to undergo validation in cooperation with ERL-C and EMSL-LV personnel. The validation procedures included a specific assessment of outlying data points for inclusion or omission in validated data sets based on assigned levels of confidence. These outliers warrant special attention or caution by the data user during analysis of the survey results. After all data were evaluated and the suspect values were confirmed or flagged, the validated data bases were frozen (Turner et al., in preparation).

Section 3

Results and Discussion

The data quality estimates presented in this section are based on the analysis of data contained in the final MASS verified data base. The parameter measurements are described with respect to their detectability, precision, accuracy, representativeness, completeness, and comparability. A summary discussion of measurement uncertainty and its relation to overall data uncertainty is also provided.

Assessment of Detectability

Data relating to detection limits for contract requirements, instrument readings, and system-wide measurement in the MASS are presented in Table 3-1. The actual reported IDLs, calculated from the calibration blanks, were less than the corresponding CRDLs for every parameter in all batches. Therefore, the MQOs for detectability in the MASS were completely satisfied. It is apparent that differences in the theoretical concentrations of DL-QCCS stock solutions among laboratories together with temporal variability of the solutions among batches and variation in the strength of acid titer solution were responsible for the high IIDLs in certain parameters, especially AC_BACL. In order to obtain lower detectability from the IIDL data, it might be necessary to contractually require the laboratories to use stricter criteria for stabilizing the strength of their DL-QCCS stock solutions. This approach could, however, preclude efforts by a particular laboratory to improve the quality of data by adopting a lower detection limit target, as was the case with Laboratory 4 in the MASS.

An issue was raised during the DDRP surveys concerning the type of QC sample that should be used in assessing instrument detectability. The calibration blank sample has been considered by some analytical chemists to be unsuitable for measurement of the IDL because the limit is based on standard deviations for a zero mg/L blank and cannot be reliably distinguished from background noise in the analytical measurement system. As an alternative, the DL-QCCS could be used to measure the IDL because the sample contains the analyte of interest at a concentration high enough to differentiate from background noise, yet low enough to be at a meaningful concentration for this assessment. Data for the DL-QCCSs from all DDRP analyses could be used to determine a more reliable MQO for instrument detectability in future surveys.

Differences between the IDLs and IIDLs for most of the other parameters were slight except for CEC_OAC, AL_CL2, SO4_PO4, SO4_0, and S_TOT. Low concentrations of aluminum in the calcium chloride extract contributed to inflation of the DL-QCCS pooled standard deviations in the zone of concentration around the CRDL. The IIDL for the SO4_PO4 parameter probably was higher because of inconsistency at the laboratories in preparing the solution standards for this parameter. Reasons for differences in the other three parameters were not clear.

The SDLs calculated from the FAL samples were much higher than either the IDLs or IIDLs, as was expected. This assessment of system-wide detectability differs from the approach taken in the two previous DDRP surveys in that low-range field audit samples were used instead of the 10 percent of field duplicate samples having the lowest concentration. Using a criterion of 80 percent or more of the routine sample concentrations exceeding the SDL as a basis for assessment, most of the parameters are suitable for all

Table 3-1. **Detection Limits for Evaluation of Contractual Compliance and for Independent Assessment of Analytical and System-Wide Measurement**

Parameter	Reporting units	Contractual compliance[a]		Independent assessment[b]		
		CRDL	IDL	IIDL	SDL	%RS>SDL[c]
CA_CL	meq/100g	0.003	0.0026	0.0032	0.1129	64.9*
MG_CL	"	0.005	0.0015	0.0018	0.0251	82.6
K_CL	"	0.002	0.0009	0.0012	0.0180	99.2
NA_CL	"	0.003	0.0012	0.0027	0.0130	40.5*
AL_CL	"	0.015	0.0111	0.0098	0.3161	93.1
CA_OAC	meq/100g	0.003	0.0022	0.0035	0.0548	76.3*
MG_OAC	"	0.005	0.0016	0.0024	0.0239	83.8
K_OAC	"	0.002	0.0009	0.0016	0.0291	96.6
NA_OAC	"	0.003	0.0010	0.0026	0.0105	59.4*
CEC_CL[d]	meq/100g	0.15	0.0530	0.1043	0.1985	100.0
CEC_CL[e]	"	0.075	0.0175	0.0116	0.2736	100.0
CEC_OAC[d]	"	0.15	0.0629	0.0785	0.4513	100.0
CEC_OAC[e]	"	0.075	0.0224	0.0055	0.2060	100.0
AC_BACL[f]	"	0.25	0.1738	0.5942	4.3067	88.3
AC_BACL[g]	"	1.25	0.6240	2.2500	—	—
CA_CL2	meq/100g	0.0050	0.0014	—	0.0861	100.0
MG_CL2	"	0.0008	0.0004	0.0003	0.0140	87.0
K_CL2	"	0.0003	0.0001	0.0001	0.0044	98.5
NA_CL2	"	0.0004	0.0002	0.0004	0.0034	95.9
FE_CL2	"	0.0005	0.0004	0.0009	0.0026	24.8*
AL_CL2	"	0.0011	0.0009	0.0031	0.0126	80.5
FE_PYP	wt %	0.005	0.0022	0.0030	0.0416	95.1
AL_PYP	"	0.005	0.0029	0.0025	0.0502	94.0
FE_AO	"	0.005	0.0023	0.0020	0.1340	78.9*
AL_AO	"	0.005	0.0036	0.0026	0.0637	94.1
SI_AO	"	0.005	0.0026	0.0023	0.0395	19.2*
FE_CD	"	0.002	0.0009	0.0007	0.0990	99.2
AL_CD	"	0.002	0.0011	0.0008	0.0272	99.4
SO4_H2O	mg S/kg	0.50	0.3339	0.4001	2.0640	95.7
SO4_PO4	"	0.50	0.3923	0.7552	3.7879	97.6
SO4_0	mg S/L	0.025	0.0167	0.0350	0.2901	88.9
C_TOT	wt %	0.010	0.0056	0.0059	0.0656	96.8
N_TOT	"	0.005	0.0015	0.0016	0.0022	99.5
S_TOT	"	0.001	0.0007	0.0021	0.0077	67.1*

[a] Contract-required detection limit and actual reported instrument detection limit, respectively, in reporting units; based on instrument analysis of calibration blanks.
[b] Independent instrument detection limit and system detection limit, respectively, in reporting units; based on analysis of DL-QCCS and FAL samples, respectively, calculated independently from the contractual requirements.
[c] Percent of routine samples with values exceeding the system detection limit (asterisk denotes fewer than 80 percent).
[d] Detection limits for the titration method (Laboratories 1 and 2 only).
[e] Detection limits for the flow injection analysis method (Laboratory 4 only).
[f] Reported for mineral samples.
[g] Reported for organic samples.
NOTE: Detection limits not applicable for physical parameters, pH, and the remaining sulfate isotherm parameters.

data uses throughout the range of concentration. The only exceptions are CA_CL and CA_OAC, NA_CL and NA_OAC, FE_CL2 and FE_AO, SI_AO, and S_TOT. Data users should use caution when assessing these parameters, as a significant portion of the routine sample concentrations are less than the corresponding SDLs and may be difficult to distinguish in regard to overall system detection and quantitation considerations. The routine sample data for NA_CL, FE_CL2, and SI_AO are particularly sensitive because less than 50 percent of the data for these parameters have concentrations greater than the corresponding SDL.

Assessment of Precision

The following tables, figures, and text provide a summary of imprecision estimates for the routine and QE sample data. The laboratory audit samples and duplicate samples were used to establish means and variabilities for pairs of theoretically identical samples. The routine samples were grouped into individual sampling class/horizon configurations in order to provide an estimate of soil heterogeneity of the regional population confounded with system-wide measurement uncertainty. The assessment of precision relates directly to the within-batch MQOs established in the MASS QA Plan (Papp et al., 1989) and to the between-batch precision that is a characteristic of the batch uncertainty introduced during sample analysis. Except for the particle size and pH parameters, the MQOs have knot values which represent the separation point for uncertainty expressed as a standard deviation (SD) in parameter reporting units for low concentrations and as a relative standard deviation (RSD) in percent for high concentrations.

The within-batch precision data are presented in sequential order of the parameters listed previously in Table 1-1 of Section 1. For each of the nine parameter groups, a table of statistics presents the QE and routine sample data below and above the knot value. Organic samples were not included in the analysis because there were insufficient degrees of freedom to make a meaningful statistical assessment of these samples. The tables show the results of the QE sample data in relation to the achievement of the precision MQOs for mineral soil samples.

Two figures are presented for each parameter within each parameter group. The first figure is a plot of the mean values and standard deviations of the LAP and LAO samples in relation to the analytical within-batch precision MQOs. From a batch acceptance standpoint, mean values below the MQO line are considered to have acceptable precision, while those values above the line had unacceptable precision. The second figure is a plot of the mean and standard deviation for each sampling class/horizon group of routine samples. The much higher variability usually observed in the routine sample data is principally a result of spatial heterogeneity among the population of soils within each sampling class/horizon group. Specifically, horizons of similarly classified soils in different sectors of the Mid-Appalachian region, e.g., Pennsylvania and Virginia, can exhibit dissimilar soil characteristics. The dissimilarities are due to subtle differences resulting from the local soil-forming factors of climate, topography, vegetation, parent material, and time.

Also included in the second figure are sets of four horizontal lines representing the within-batch standard deviations for the field duplicates and preparation duplicates and the within- and between-batch standard deviations for the laboratory audit samples. Each set of lines represents the imprecision estimates within the partitioned intervals established by the step function across the entire range of concentration (see Appendix C). It is assumed that the intervals within each concentration range are independent of the type of measurement quality sample represented, even though there are subtle differences in the distributions of the samples. The primary purpose of this figure is to show the contribution of measurement imprecision to the overall variability of the routine sample data.

A data table corresponding to the step function statistical procedure applied to each parameter is given in Appendix C as supplemental information for the derivation of the precision data provided in the plots. Appendix D presents data, sorted by data set, that identify QE or routine samples having inordinately high or low values that exert a disproportionate influence on the overall data quality. These data may be of interest to data users during the evaluation of specific data sets represented in the plots or of individual batches of samples from a given analytical laboratory.

Moisture and Particle Size Analyses

The analytical, preparation, and field within-batch precision MQOs were satisfied for the MOIST, SAND, SILT, and CLAY parameters (see Table 3-2). The individual sand and silt separates, i.e., fractions, were not subjected to the batch acceptance criteria used with the MQOs; hence, the precision of the separates were not used as a basis for satisfying the particle size precision objectives (see Appendix E). Particle size analyses were not performed on organic soil samples because the inorganic component for which these analyses were designed was low or absent in many of these soils. With few exceptions, a general pattern of increasing standard deviation with increased sources of confounded error was observed, i.e., the standard deviation from the field duplicate samples exceeded that of the preparation duplicate and laboratory audit samples.

The upward adjustment of the particle size analytical MQOs from 1.0 weight percent in the two previous DDRP surveys to 3.0 weight percent for SAND and SILT and 2.0 weight percent for CLAY in the MASS appeared to compensate for error in horizons dominated by one particle size fraction. Therefore, the less stringent MQOs are considered to be reasonable expectations for laboratory and system-wide performance for particle size analysis.

Imprecision was much lower for COSI and FSI in the duplicate samples compared to the laboratory audit samples despite the increasing sources of error. Also, the audit sample imprecision for these parameters was much higher than the corresponding SILT values. The source of this uncertainty was investigated and found to be the result of apparent difficulties with particle size analysis at Laboratory 2, which had not been using a 270-mesh sieve at the bottom of the nested sieves during the early stages of batch analysis. Inordinate COSI and FSI values for a LAP sample in Batch 30106 were responsible for the higher imprecision, although the precision for SILT (the silt parameter of primary interest to the data users) was acceptable. The initial run and two reanalysis runs of particle size on this batch provided mixed results for different particle size fractions, and it was determined that the second run had the most consistent analytical results even though the COSI and

Table 3-2. Achievement of Measurement Quality Objectives for Within-Batch Precision of Moisture and Particle Size Analysis

Data set[a]	Parameter	df[b]	SD[c]	MQO[c]	Pairs>MQO	
			—— wt % ——		n	%
LAP	MOIST	27	0.2157	0.3	5	18.5
	SAND	27	1.1596	3.0	0	0.0
	VCOS	27	0.9116			
	COS	27	0.6642			
	MS	27	0.7921			
	FS	27	0.5946			
	VFS	27	0.6654			
	SILT	27	1.8783	3.0	2	7.4
	COSI	27	4.0549			
	FSI	27	4.3368			
	CLAY	27	1.1304	2.0	1	3.7
PD	MOIST	54	0.0707	0.3	0	0.0
	SAND	54	1.2519	3.0	2	3.7
	VCOS	54	1.5450			
	COS	54	0.8262			
	MS	54	0.5127			
	FS	54	0.7940			
	VFS	54	0.8538			
	SILT	54	1.1904	3.0	2	3.7
	COSI	54	0.9284			
	FSI	54	1.0083			
	CLAY	54	0.6661	2.0	1	1.9
FD	MOIST	27	0.1160	0.3	0	0.0
	SAND	27	2.6239	6.0	1	3.7
	VCOS	27	2.0730			
	COS	27	1.1546			
	MS	27	0.8578			
	FS	27	0.9184			
	VFS	27	1.1540			
	SILT	27	2.0266	6.0	1	3.7
	COSI	27	1.1717			
	FSI	27	1.3155			
	CLAY	27	1.1231	4.0	0	0.0
S/H	MOIST	618	0.6505			
	SAND	618	14.2599			
	VCOS	618	4.0964			
	COS	618	4.3134			
	MS	618	6.3679			
	FS	618	7.9281			
	VFS	618	4.8732			
	SILT	618	10.2112			
	COSI	618	5.2974			
	FSI	618	7.7111			
	CLAY	618	7.3806			

[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviation and measurement quality objective, respectively, expressed in weight percent for mineral soil samples; a knot point of 12.0 weight percent was specified for MOIST, although no data were observed in the upper tier.

FSI fractions were erroneous for the LAP samples. As a secondary check on the quality of the batch routine sample data, the outputs from each run were compared. With the exception of the LAP samples, the silt values for all samples in the batch were similar across runs and did not warrant concern for batch-wide data quality. The QA staff concluded that the overall precision for COSI and FSI is actually much better than portrayed due to the inordinate effect of the LAP samples in Batch 30106.

Figures 3-1 through 3-4 are plots of the laboratory audit sample data in relation to the within-batch precision MQOs and of the routine sample data in relation to selected QE samples. The plots are provided only for those physical parameters for which MQOs were defined, i.e., for MOIST, SAND, SILT, and CLAY. Appendix E contains the routine data plots for the remaining particle size parameters. Supplemental information regarding uncertainty estimates is presented in Appendix C, and the identification of inordinate data values is presented in Appendix D.

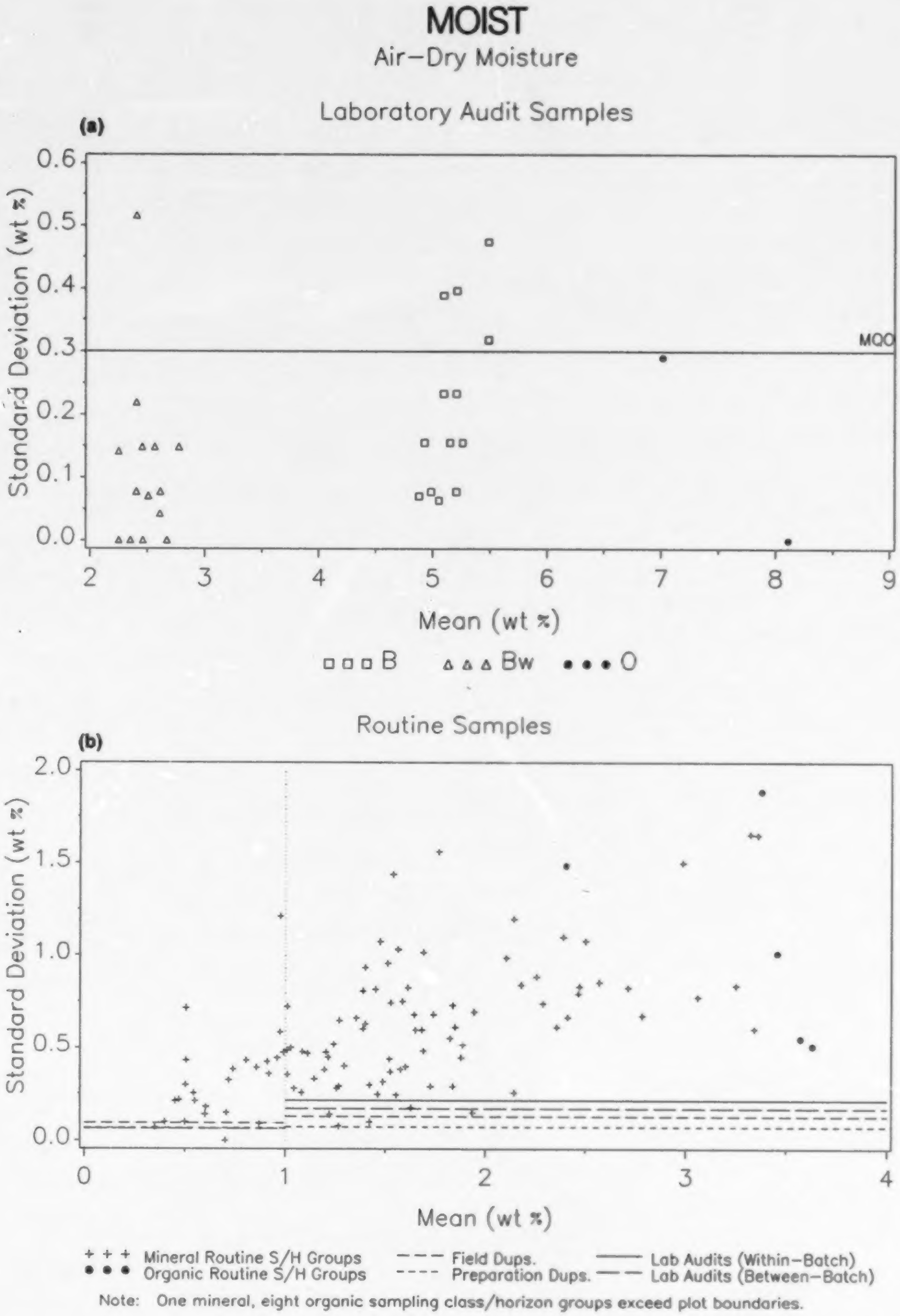


Figure 3-1. Range and frequency distribution of MOIST for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

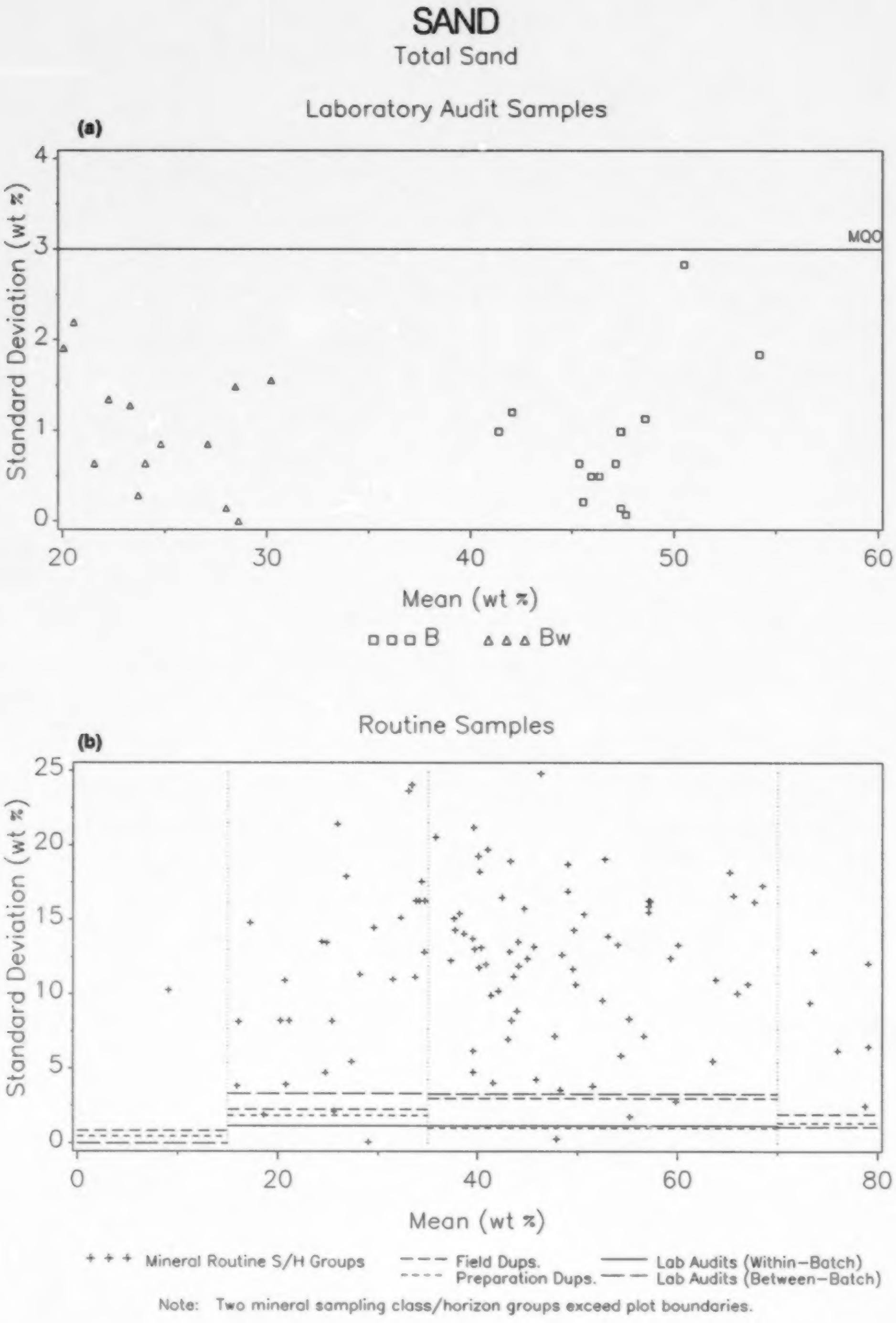


Figure 3-2. Range and frequency distribution of SAND for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

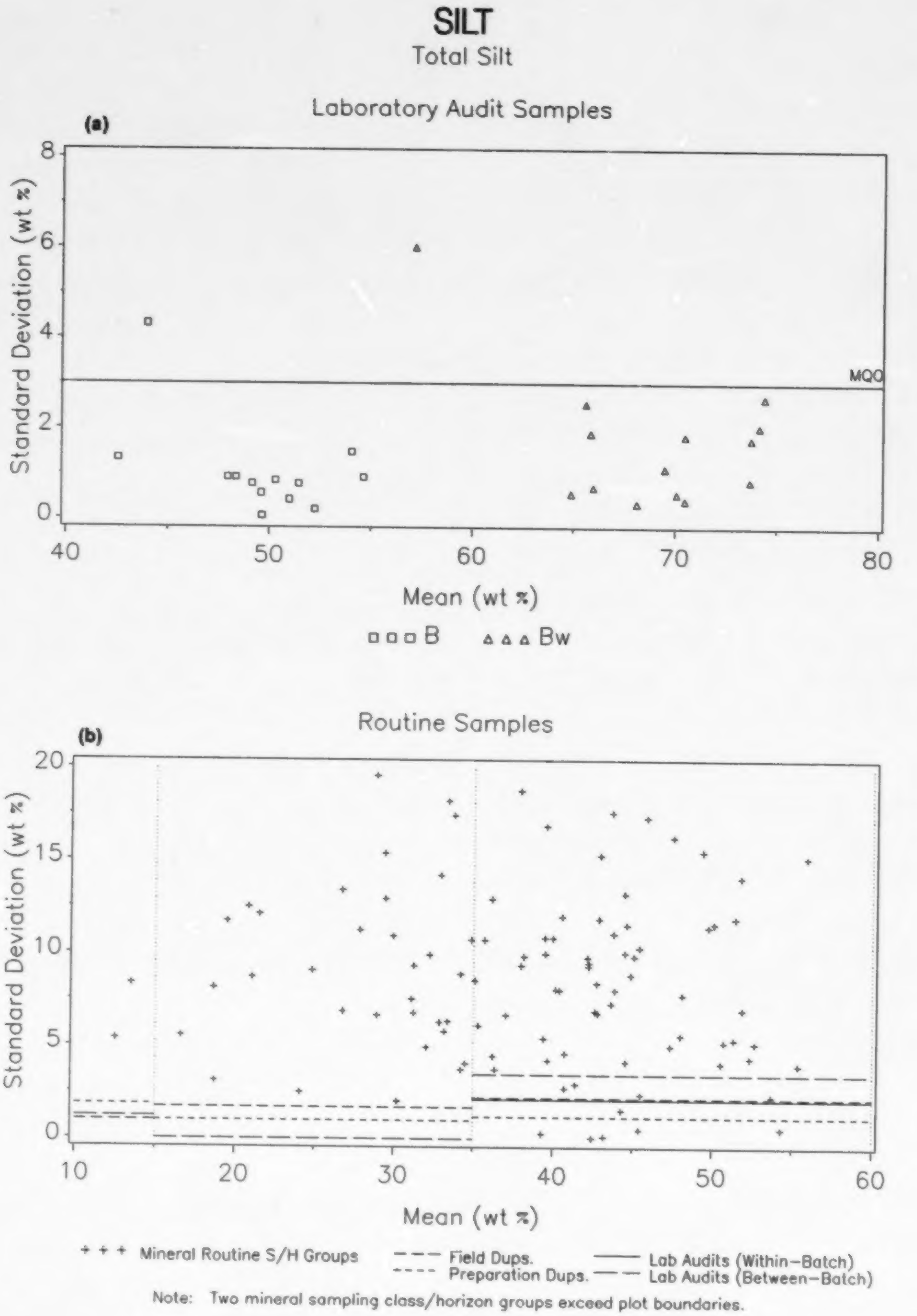
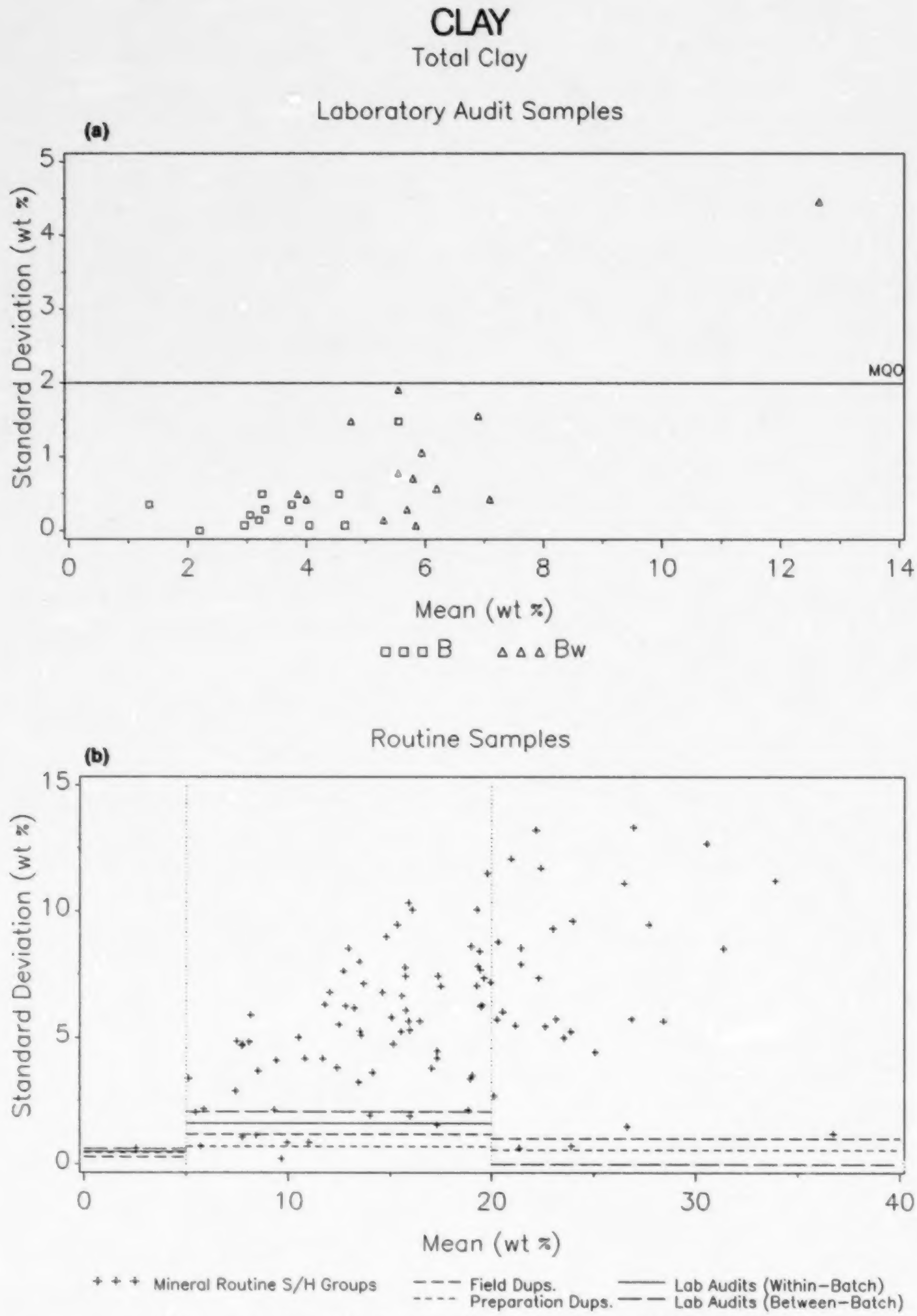


Figure 3-3. Range and frequency distribution of SILT for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: Three mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-4. **Range and frequency distribution of CLAY for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.**

Soil pH

The analytical, preparation, and field within-batch precision MQOs were satisfied for each of the three soil pH parameters (see Table 3-3). A general pattern of increasing standard deviation with increased sources of confounded error was maintained for each parameter. The standard deviation showed a slight change over the measured pH range and it was necessary to apply the step function to the data.

Figures 3-5 through 3-7 are plots of the laboratory audit sample data in relation to the within-batch precision MQOs and of the routine sample data in relation to selected QE samples. Supplemental information regarding uncertainty estimates is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-3. Achievement of Measurement Quality Objectives for Within-Batch Precision of Soil pH

Data set[a]	Parameter	df[b]	SD[c]	MQO[c]	Pairs>MQO	
			--- pH units ---		n	%
LAP	PH_H2O	27	0.0525	0.10	3	11.1
	PH_002M	27	0.0518	0.10	1	3.7
	PH_01M	27	0.0319	0.10	0	0.0
PD	PH_H2O	54	0.0563	0.10	4	7.4
	PH_002M	54	0.0599	0.10	1	1.9
	PH_01M	54	0.0345	0.10	0	0.0
FD	PH_H2O	27	0.0939	0.20	1	3.7
	PH_002M	27	0.1017	0.20	2	7.4
	PH_01M	27	0.0667	0.20	0	0.0
S/H	PH_H2O	618	0.4756			
	PH_002M	618	0.4562			
	PH_01M	618	0.4352			

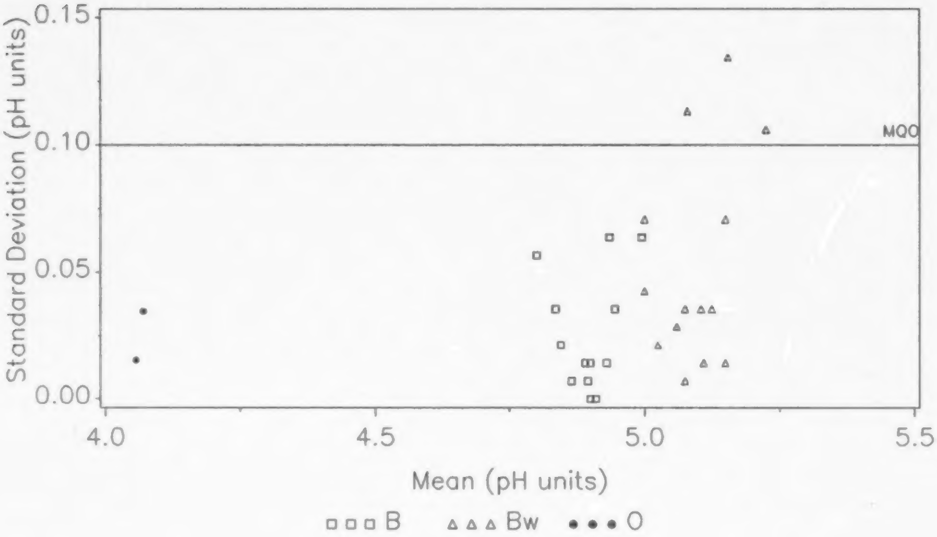
[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

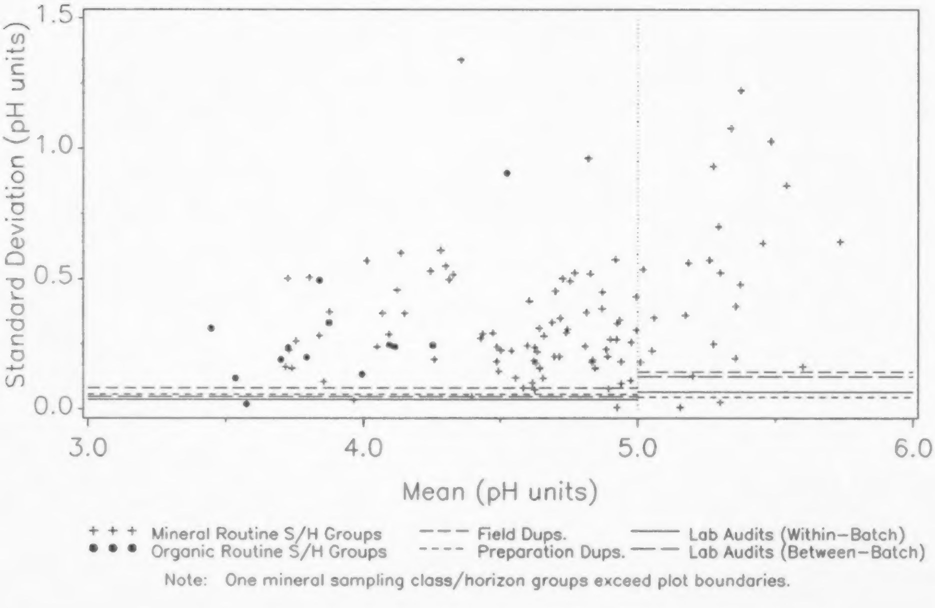
[c] Standard deviations expressed in pH units for mineral soil samples.

PH_H2O
pH in Water

(a) Laboratory Audit Samples



(b) Routine Samples



Note: One mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-5. Range and frequency distribution of PH_H20 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estim.

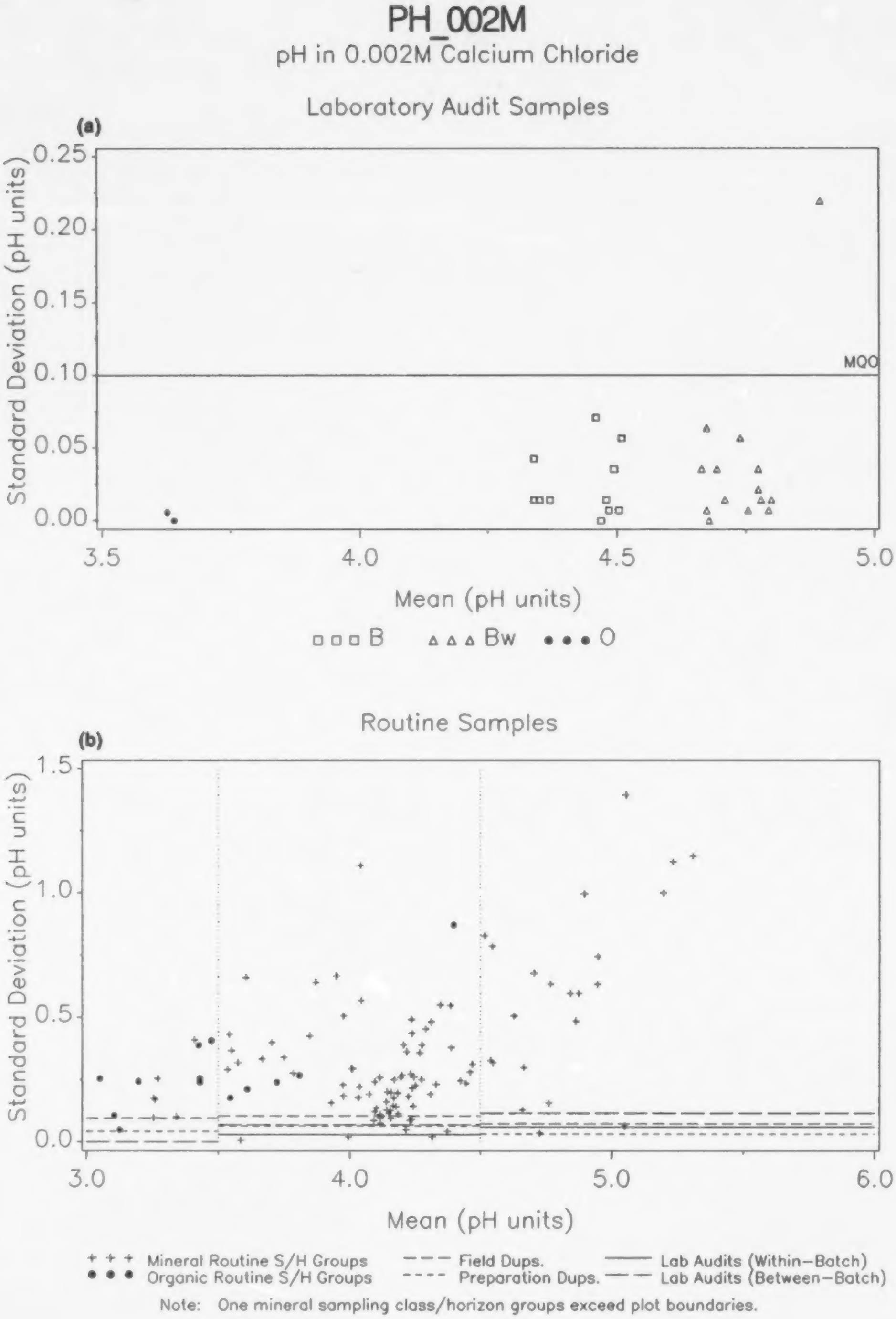
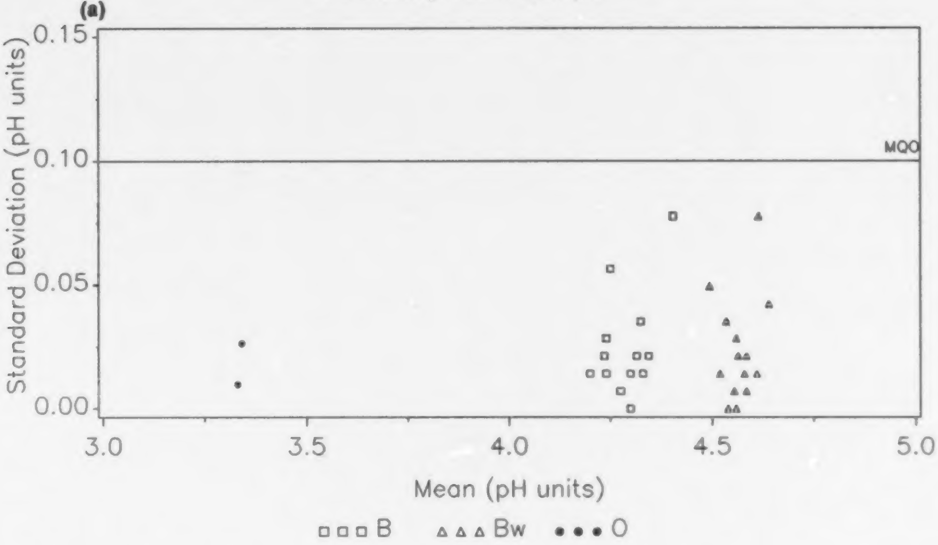


Figure 3-6. **Range and frequency distribution of PH_002M for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.**

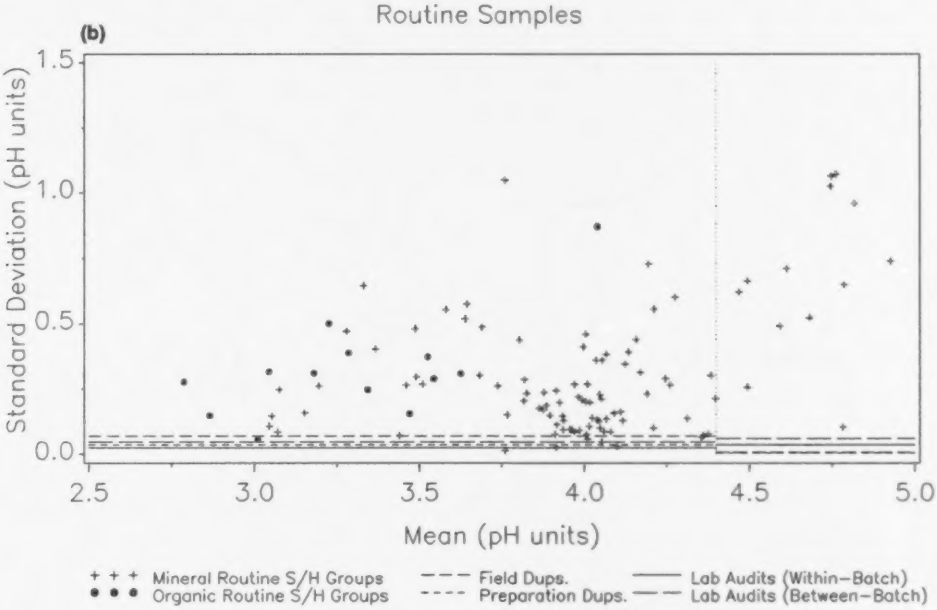
PH_01M

pH in 0.01M Calcium Chloride

Laboratory Audit Samples



Routine Samples



Note: One mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-7. Range and frequency distribution of PH_01M for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates

Exchangeable Cations in Ammonium Chloride

The analytical within-batch precision MQOs were satisfied for all of the cations in ammonium chloride except for AL_CL above the knot (see Table 3-4). The MQOs were less stringent for this cation because it was a new parameter that was not measured in the previous DDRP surveys. However, the effect of data from two of the 27 audit sample pairs in the upper tier caused an inordinate increase in the uncertainty to 15.8 percent which slightly exceeded the MQO. The imprecision estimates for the preparation and field duplicates were not affected by inordinate AL_CL data and easily satisfied their respective MQOs. Therefore, it is likely that an upper tier precision objective of 10 percent for the laboratory audit samples can be satisfied in most cases when using protocols and acceptance criteria identical to those used to measure AL_CL in the MASS. Likewise, a lower tier objective of 0.10 meq/100g can probably be satisfied for the same parameter.

The field within-batch imprecision for CA_CL, while achieving the MQOs for both tiers, was high in relation to the other cations of the ammonium chloride extract and in relation to the imprecision observed in the laboratory audit samples and preparation duplicates. The pattern was also noted for CA_OAC in the ammonium acetate extraction, as described later in this section. Because of this apparent incongruity in the precision data, the possibility of selective sample contamination during the field sampling or preparation laboratory operations was investigated. There was no evidence to suggest a contamination problem; therefore, the original SCS-SOI-232 field data forms were checked to determine whether there was a pedon-specific reason for the variability of particular inordinate field duplicates. The field duplicate/routine pair for

Table 3-4. Achievement of Measurement Quality Objectives for Within-Batch Precision of the Exchangeable Cations in Ammonium Chloride

		Below the knot[c]					Above the knot[c]				
Data set[a]	Parameter	df[b]	SD	MQO	Pairs>MQO n	Pairs>MQO %	df	RSD	MQO	Pairs>MQO n	Pairs>MQO %
			– meq/100g –					—— % ——			
LAP	CA_CL	.	.	0.02	.	.	27	6.8	10	2	7.4
	MG_CL	27	0.0116	0.02	1	3.7	.	.	10	.	.
	K_CL	27	0.0040	0.02	0	0.0	.	.	10	.	.
	NA_CL	27	0.0056	0.02	0	0.0	.	.	10	.	.
	AL_CL	.	.	0.20	.	.	27	15.8	15	2	7.4
PD	CA_CL	32	0.0074	0.02	0	0.0	22	6.7	15	1	4.5
	MG_CL	46	0.0128	0.02	2	4.3	8	5.2	15	0	0.0
	K_CL	54	0.0051	0.02	0	0.0	.	.	15	.	.
	NA_CL	50	0.0035	0.02	0	0.0	.	.	15	.	.
	AL_CL	3	0.0345	0.20	0	0.0	51	6.1	22	0	0.0
FD	CA_CL	17	0.0430	0.04	2	11.8	10	23.9	30	1	10.0
	MG_CL	23	0.0136	0.04	0	0.0	4	4.8	30	0	0.0
	K_CL	27	0.0055	0.04	0	0.0	.	.	30	.	.
	NA_CL	25	0.0045	0.04	0	0.0	.	.	30	.	.
	AL_CL	1	0.0233	0.40	0	0.0	26	6.7	45	0	0.0
S/H	CA_CL	108	0.1487				510	142.2			
	MG_CL	302	0.2219				316	117.6			
	K_CL	542	0.0661				76	116.3			
	NA_CL	618	0.0131				.	.			
	AL_CL	3	0.6176				615	59.3			

[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in meq/100g and percent, respectively, for mineral soil samples below and above the knot point of 0.20 meq/100g (1.3 meq/100g for AL_CL); a dot signifies a lack of data occupying that range.

Batch 30113 was collected from an abandoned cropland site that had been previously limed, hence, it is possible that lime was irregularly distributed in the horizon and contributed to the high observed variability in calcium. It was also suspected that the field duplicate/routine pair for Batch 30128 was in some way affected by a sample switch for the cation analyses even though the QART did not justify a batch-wide reanalysis to address this discrepancy. If the effect of these two inordinate pairs was removed from the precision assessment, the field duplicate estimates would be comparable with the other measurement quality samples.

There was a general trend of increasing standard deviation with increased sources of confounded error. The imprecision estimates for the preparation duplicates were about the same as for the laboratory audit samples and were somewhat less than the field duplicates.

Figures 3-8 through 3-12 are plots of the laboratory audit sample data in relation to the within-batch MQOs and of the routine sample data in relation to selected QE samples. Supplemental information regarding uncertainty estimates is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

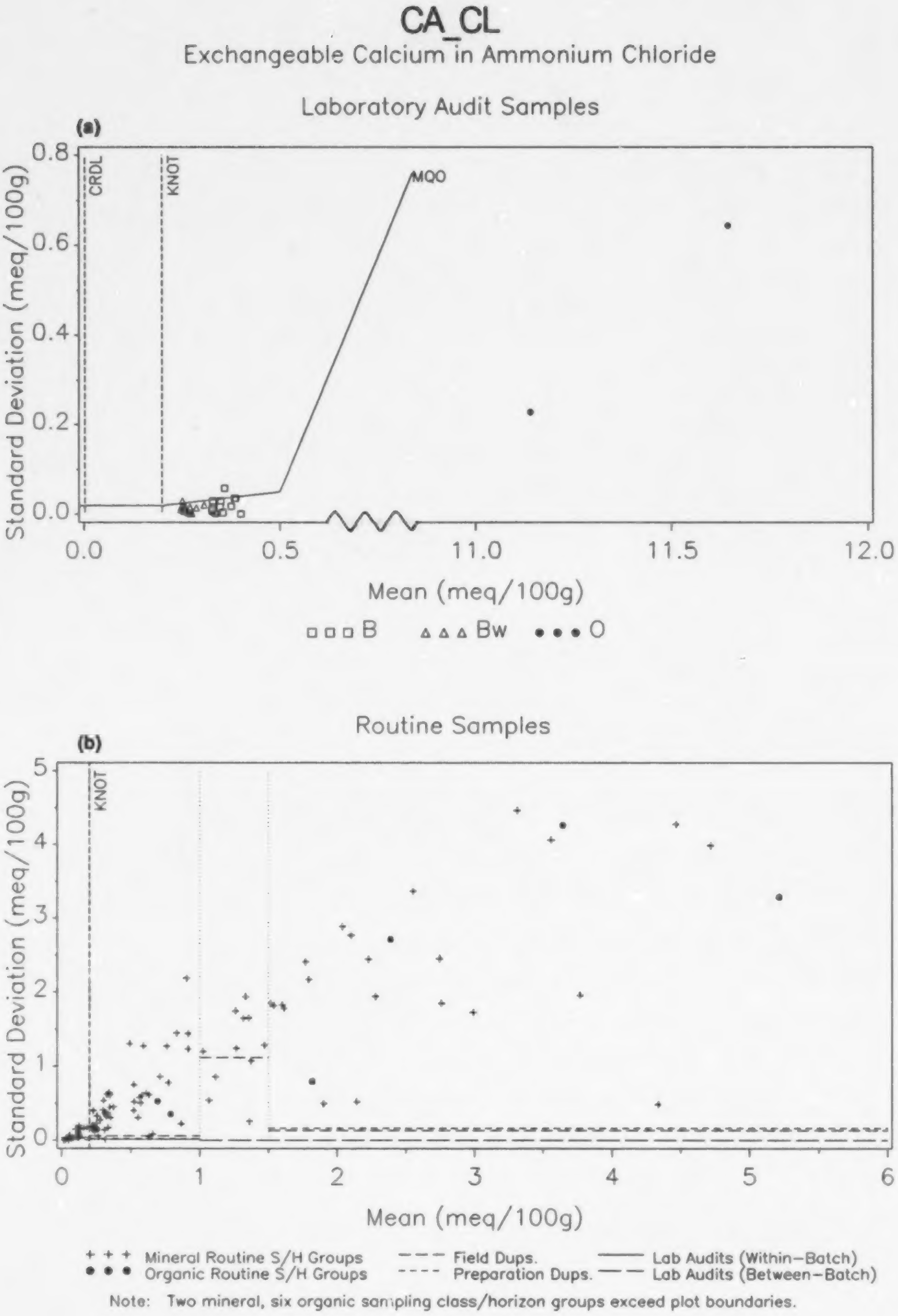
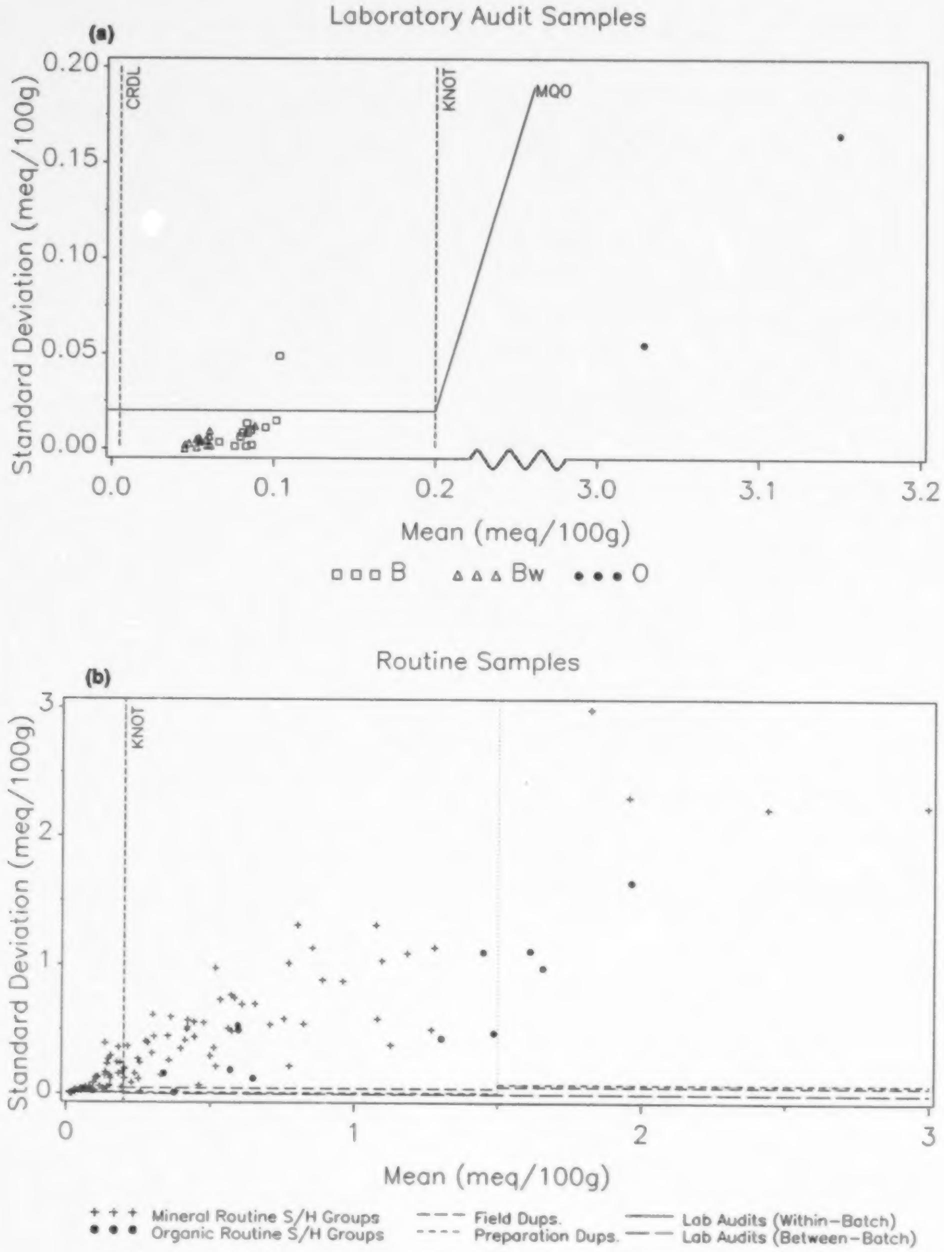


Figure 3-8. **Range and frequency distribution of CA_CL for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.**

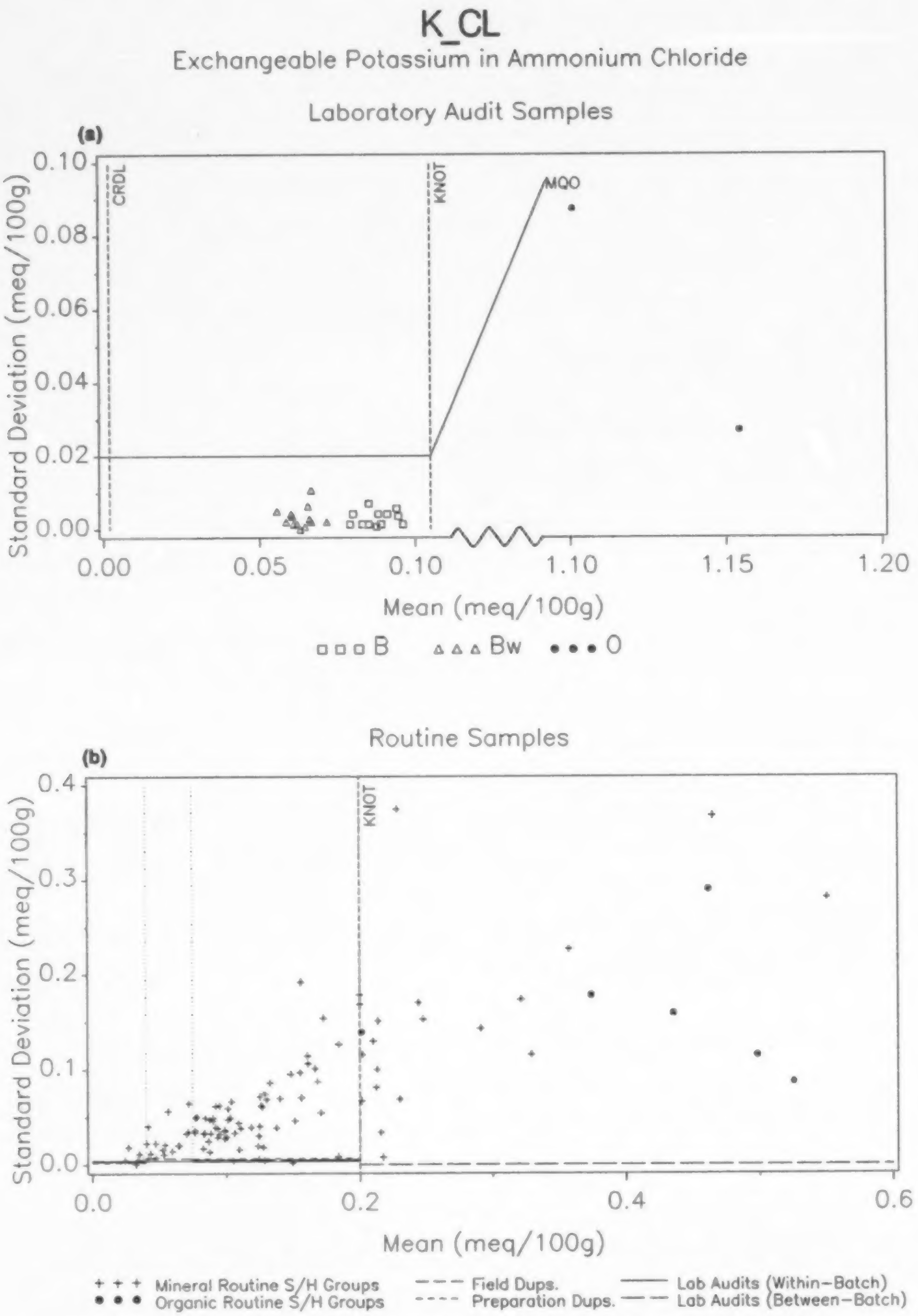
MG_CL

Exchangeable Magnesium in Ammonium Chloride



Note: One mineral, one organic sampling class/horizon groups exceed plot boundaries.

Figure 3-9. Range and frequency distribution of MG_CL for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

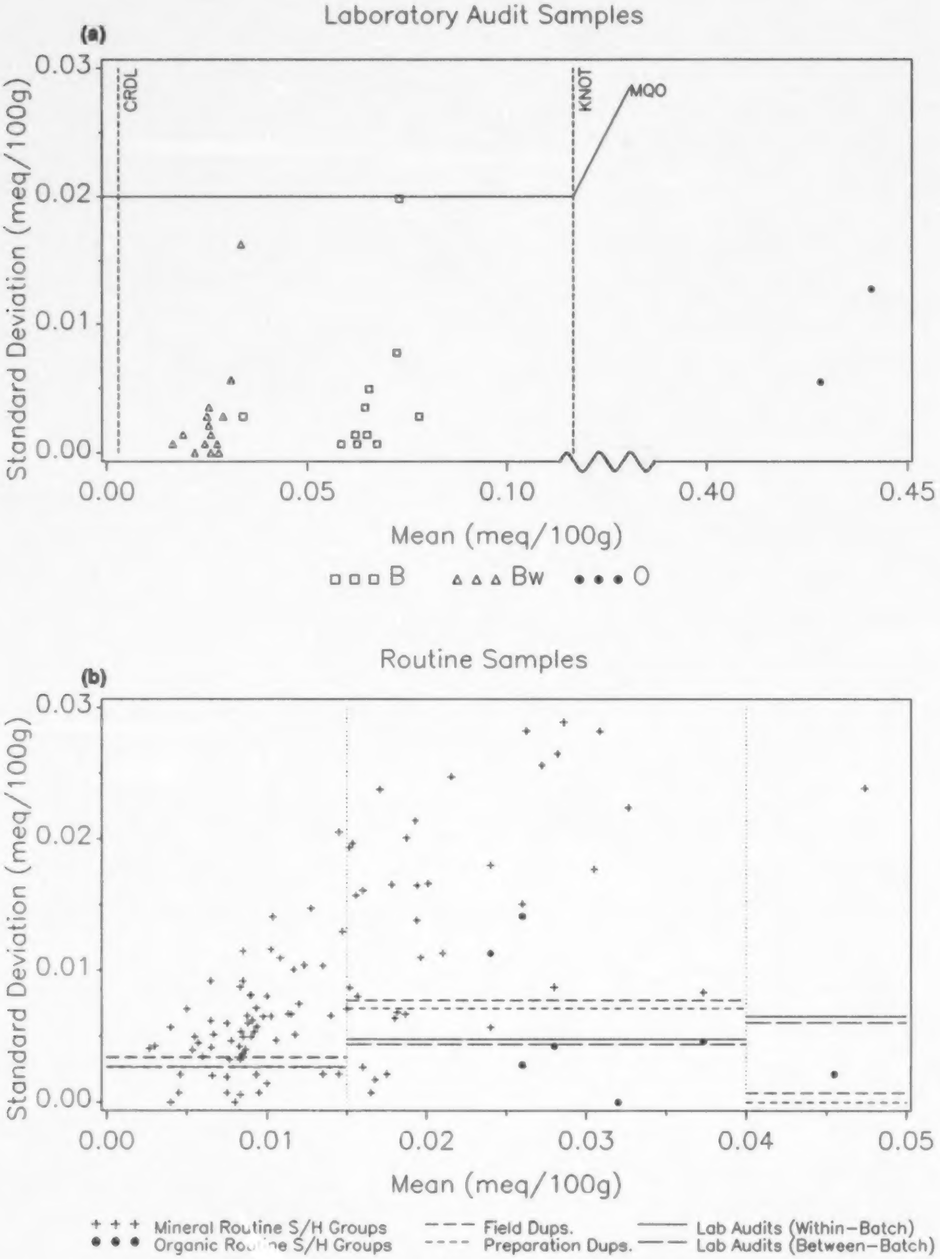


Note: Two mineral, seven organic sampling class/horizon groups exceed plot boundaries.

Figure 3-10. Range and frequency distribution of K_CL for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

NA_CL

Exchangeable Sodium in Ammonium Chloride

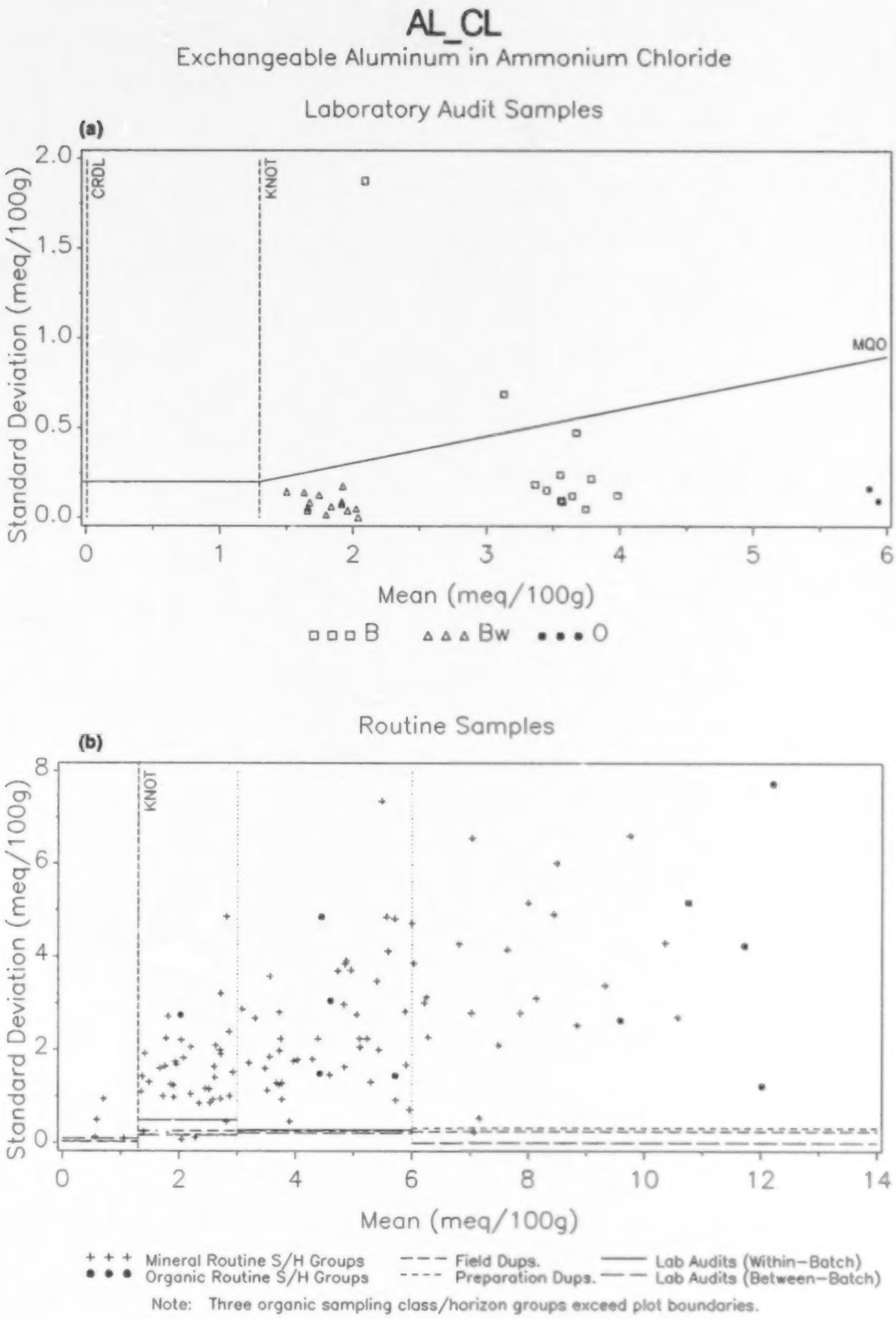


Laboratory Audit Samples

Routine Samples

Note: Three mineral, six organic sampling class/horizon groups exceed plot boundaries.

Figure 3-11. Range and frequency distribution of NA_CL for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.


AL_CL

Exchangeable Aluminum in Ammonium Chloride

Laboratory Audit Samples

Routine Samples

Note: Three organic sampling class/horizon groups exceed plot boundaries.

Figure 3-12. Range and frequency distribution of AL_CL for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

Exchangeable Cations in Ammonium Acetate

The analytical and preparation within-batch precision MQOs were satisfied for the exchangeable cations in ammonium acetate (see Table 3-5). A general pattern of increasing standard deviation with increased sources of confounded error was maintained.

The field within-batch imprecision for CA_OAC barely satisfied the MQO for the lower tier and slightly exceeded the MQO for the upper tier, and was high in relation to the other cations of the ammonium acetate extract and in relation to the imprecision observed in the laboratory audit samples and preparation duplicates. The pattern was also noted for CA_CL in the ammonium chloride extraction, as described previously in this section. Because of this apparent incongruity in the precision data, the possibility of selective sample contamination during the field sampling or preparation laboratory operations was investigated. There was no evidence to suggest a contamination problem, therefore, the original SCS-SOI-232 field data forms were checked to determine whether there was a pedon-specific reason for the variability of particular inordinate field duplicates. The field duplicate/routine pair for Batch 30113 was collected from an abandoned cropland site that had been previously limed, hence, it is possible that lime was irregularly distributed in the horizon and contributed to the high observed variability in calcium. It was also suspected that the field duplicate/routine pair for Batch 30128 was in some way affected by a sample switch for the cation analyses even though the QART did not justify a batch-wide reanalysis to address this discrepancy. Removing the effect of these two inordinate pairs from the precision assessment makes the field duplicate estimates comparable with the other measurement quality samples.

Figures 3-13 through 3-16 are plots of the laboratory audit sample data in relation to the within-batch MQOs and of the routine sample data in relation to selected QE samples. Supplemental information regarding uncertainty estimates is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-5. Achievement of Measurement Quality Objectives for Within-Batch Precision of the Exchangeable Cations in Ammonium Acetate

Data set[a]	Parameter	Below the knot[c]					Above the knot[c]				
		df[b]	SD – meq/100g –	MQO – meq/100g –	Pairs>MQO n	Pairs>MQO %	df	RSD — % —	MQO — % —	Pairs>MQO n	Pairs>MQO %
LAP	CA_OAC	.	.	0.02	.	.	27	9.1	10	4	14.8
	MG_OAC	27	0.0142	0.02	3	11.1	.	.	10	.	.
	K_OAC	27	0.0053	0.02	0	0.0	.	.	10	.	.
	NA_OAC	54	0.0050	0.02	0	0.0	.	.	10	.	.
PD	CA_OAC	33	0.0070	0.02	2	6.1	21	9.5	15	2	9.5
	MG_OAC	46	0.0095	0.02	3	6.5	8	3.3	15	0	0.0
	K_OAC	51	0.0081	0.02	2	3.9	3	7.1	15	0	0.0
	NA_OAC	59	0.0032	0.02	0	0.0	.	.	15	.	.
FD	CA_OAC	18	0.0394	0.04	3	16.7	9	33.3	30	2	22.2
	MG_OAC	23	0.0143	0.04	0	0.0	4	5.6	30	0	0.0
	K_OAC	25	0.0067	0.04	0	0.0	2	8.0	30	0	0.0
	NA_OAC	29	0.0043	0.04	0	0.0	.	.	30	.	.
S/H	CA_OAC	113	0.1457				505	143.1			
	MG_OAC	301	0.2162				317	116.2			
	K_OAC	545	0.0640				73	111.2			
	NA_OAC	754	0.0147				.	.			

[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in meq/100g and percent, respectively, for mineral soil samples below and above the knot point of 0.20 meq/100g; a dot signifies a lack of data occupying that range.

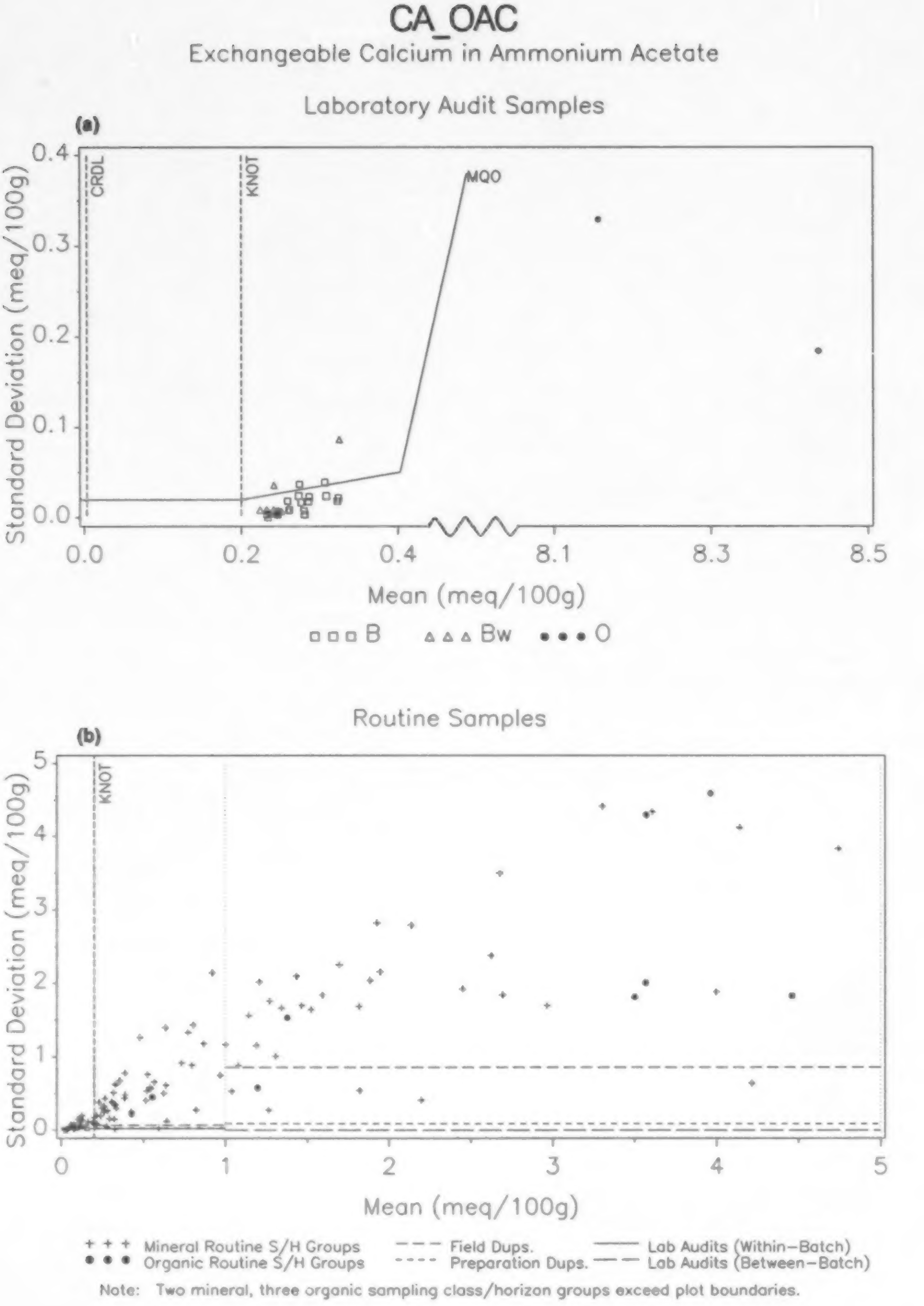
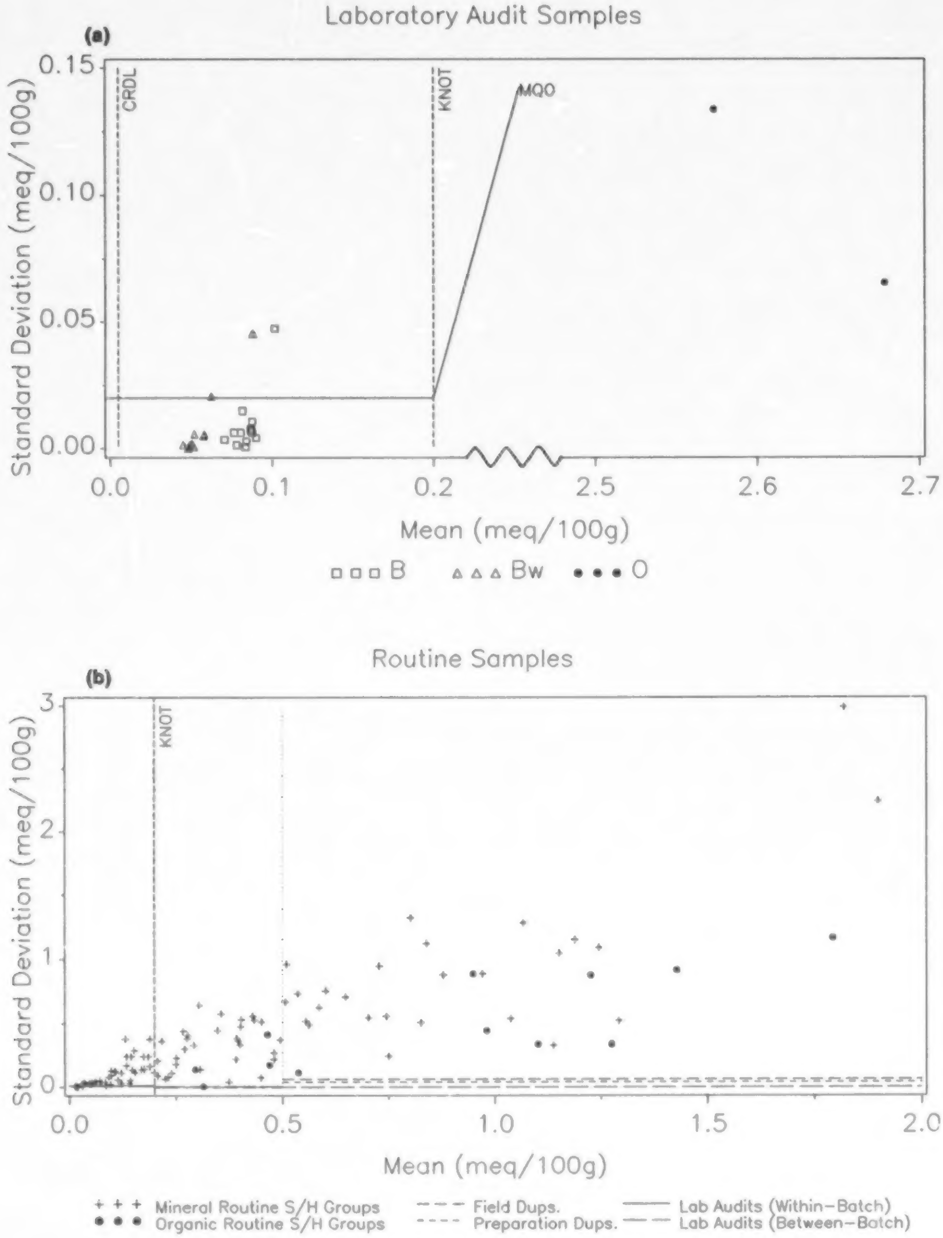


Figure 3-13. Range and frequency distribution of CA_OAC for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

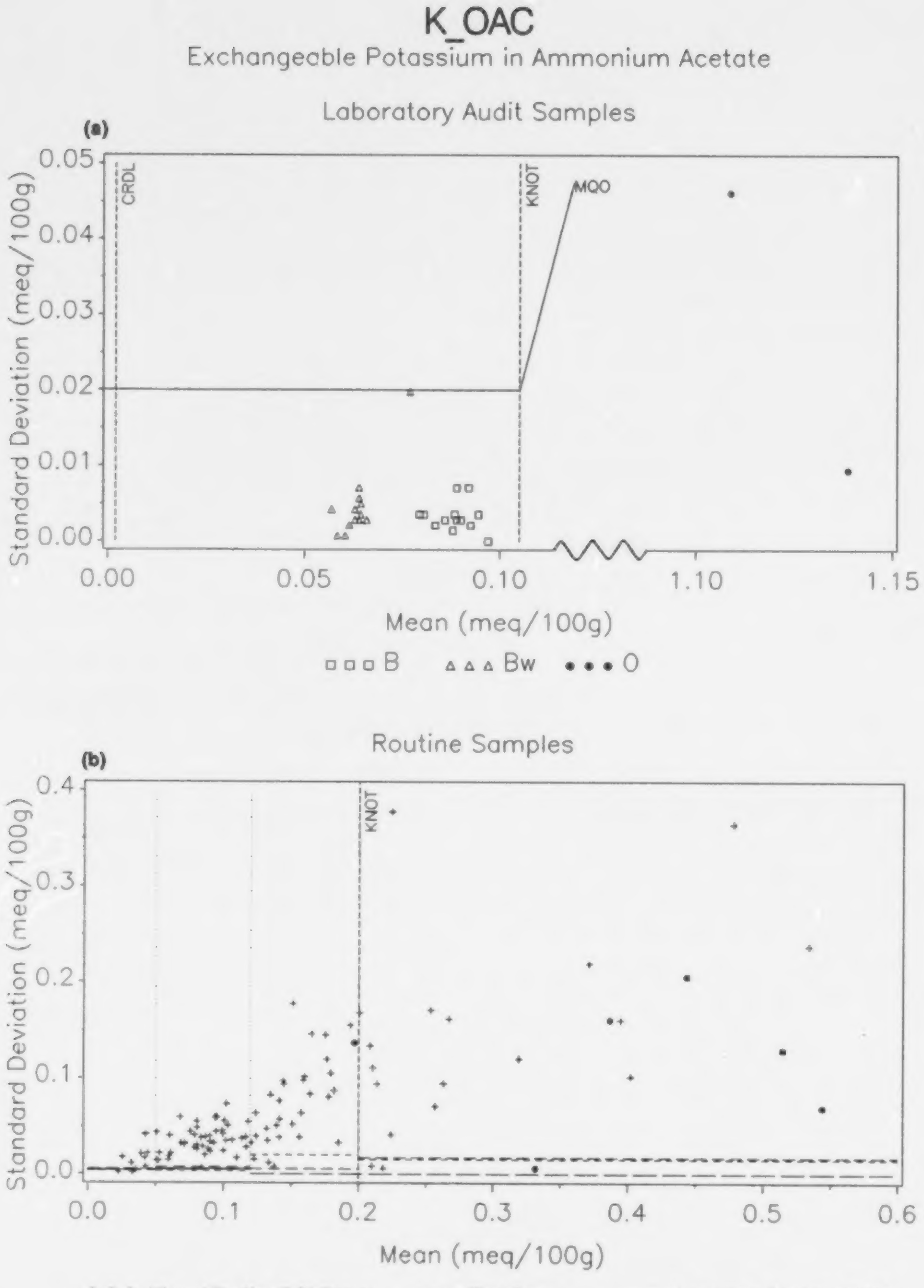
MG_OAC

Exchangeable Magnesium in Ammonium Acetate



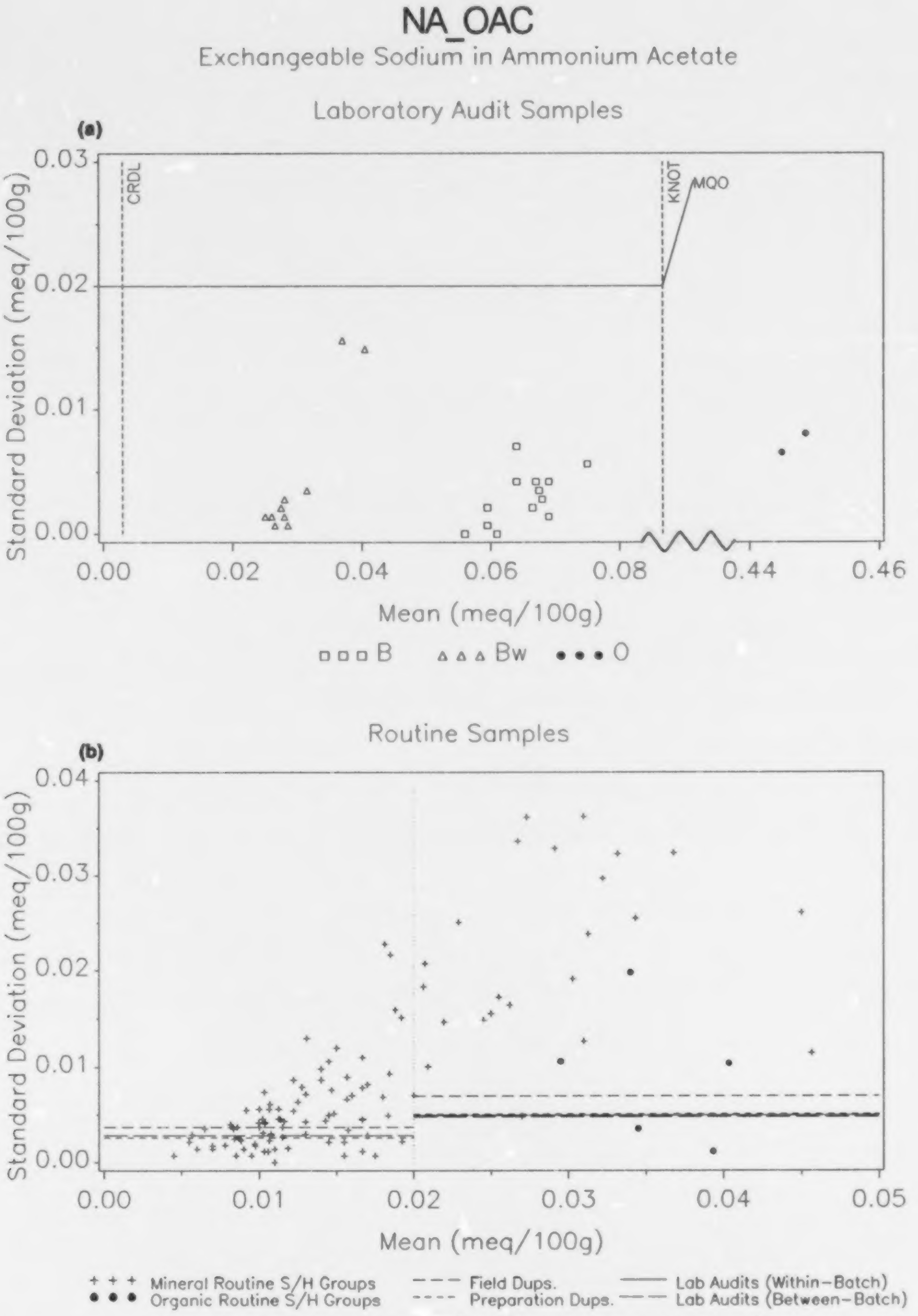
Note: Three mineral, one organic sampling class/horizon groups exceed plot boundaries.

Figure 3-14. Range and frequency distribution of MG_OAC for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: Two mineral, seven organic sampling class/horizon groups exceed plot boundaries.

Figure 3-15. Range and frequency distribution of K_OAC for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: Eight organic sampling class/horizon groups exceed plot boundaries.

Figure 3-16. Range and frequency distribution of NA_OAC for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

Cation Exchange Capacity and Exchangeable Acidity

The analytical, preparation, and field within-batch precision MQOs were satisfied for the CEC and exchangeable acidity parameters (see Table 3-6). There was a general trend of increasing standard deviation with increased sources of confounded error for all parameters.

Figures 3-17 through 3-19 are plots of the laboratory audit sample data in relation to the within-batch MQOs and of the routine sample data in relation to selected QE samples. Supplemental information regarding uncertainty estimates is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

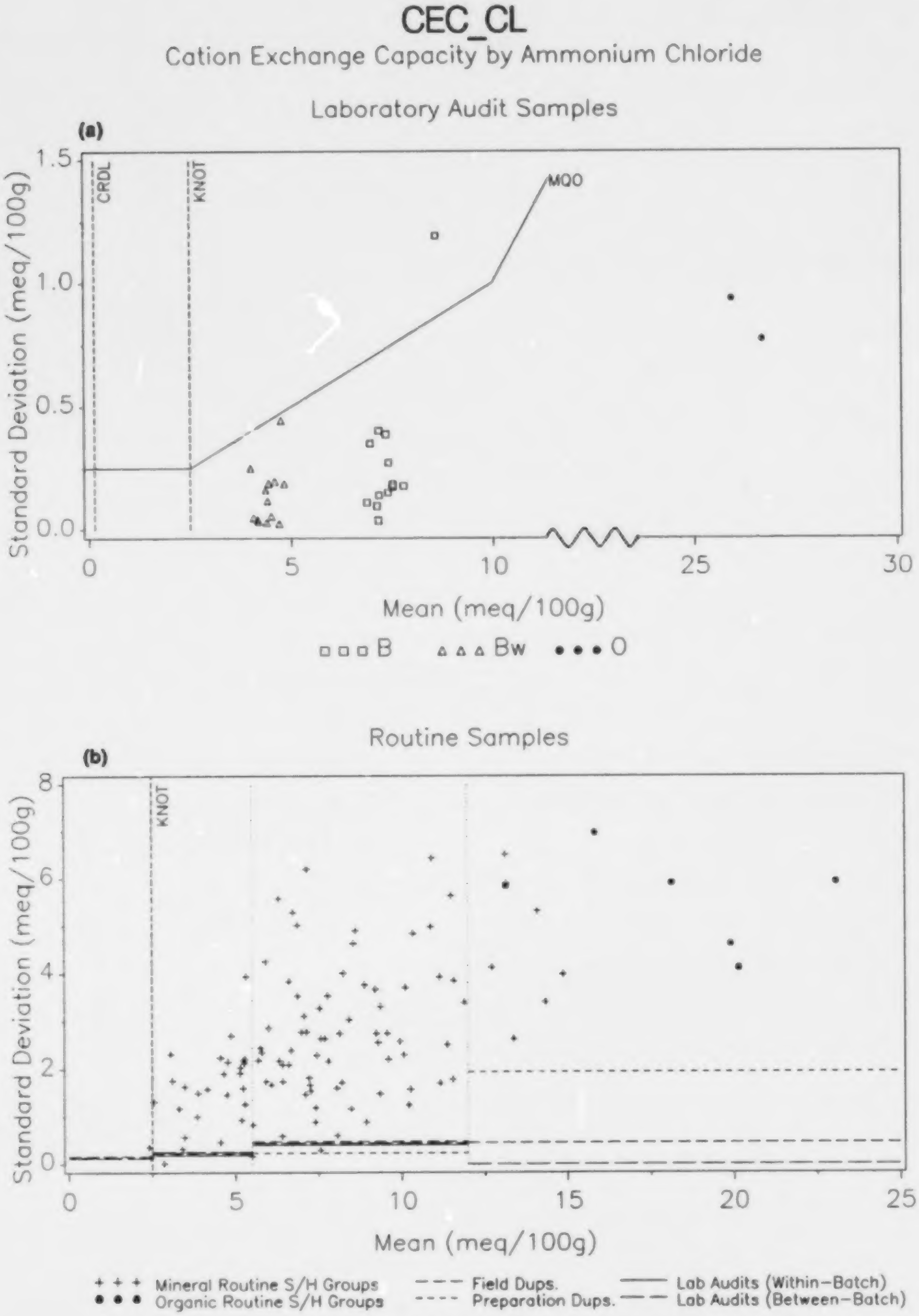
Table 3-6. Achievement of Measurement Quality Objectives for Within-Batch Precision of Cation Exchange Capacity and Exchangeable Acidity

		Below the knot[c]					Above the knot[c]				
Data set[a]	Parameter	df[b]	SD	MQO	Pairs>MQO		df	RSD	MQO	Pairs>MQO	
			– meq/100g –		n	%		------ %------		n	%
LAP	CEC_CL	.	.	0.25	.	.	27	5.2	10	1	3.7
	CEC_OAC	.	.	0.25	.	.	27	6.5	10	2	7.4
	AC_BACL	.	.	1.00	.	.	27	6.2	15	1	3.7
PD	CEC_CL	3	0.1389	0.25	0	0.0	51	9.0	15	2	3.9
	CEC_OAC	.	.	0.25	.	.	54	11.1	15	5	9.3
	AC_BACL	19	0.6044	1.00	1	5.3	35	8.9	22	0	0.0
FD	CEC_CL	1	0.1648	0.50	0	0.0	26	5.5	30	0	0.0
	CEC_OAC	.	.	0.50	.	.	27	11.3	30	1	3.7
	AC_BACL	11	0.9879	2.00	0	0.0	16	9.4	45	0	0.0
S/H	CEC_CL	4	0.2681				614	39.0			
	CEC_OAC	.	.				618	42.5			
	AC_BACL	131	3.3224				487	46.6			

[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in meq/100g and percent, respectively, for mineral soil samples below and above the knot point of 2.5 meq/100g (6.7 meq/100g for AC_BACL); a dot signifies a lack of data occupying that range.



Note: One mineral, seven organic sampling class/horizon groups exceed plot boundaries.

Figure 3-17. Range and frequency distribution of CEC_CL for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

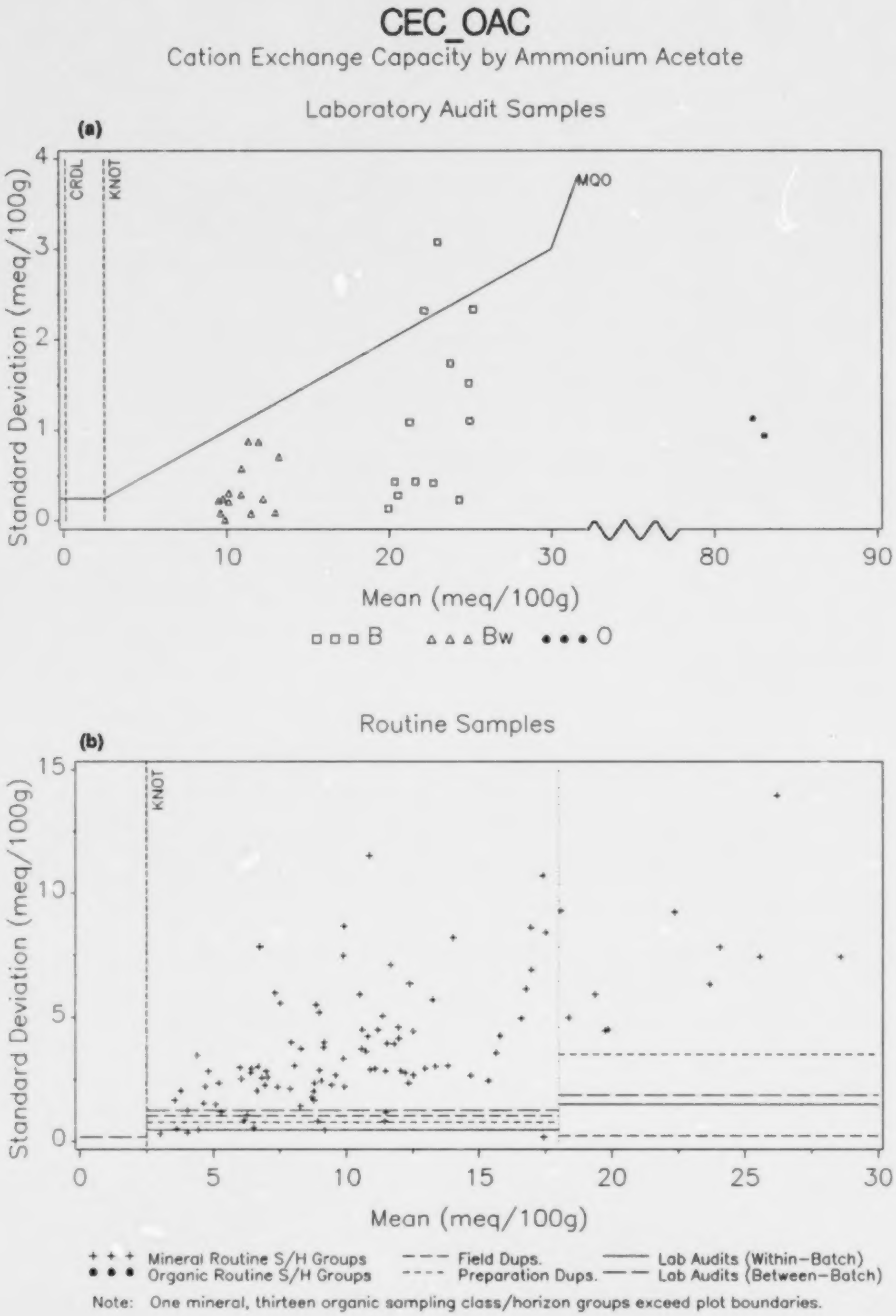


Figure 3-18. Range and frequency distribution of CEC_OAC for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

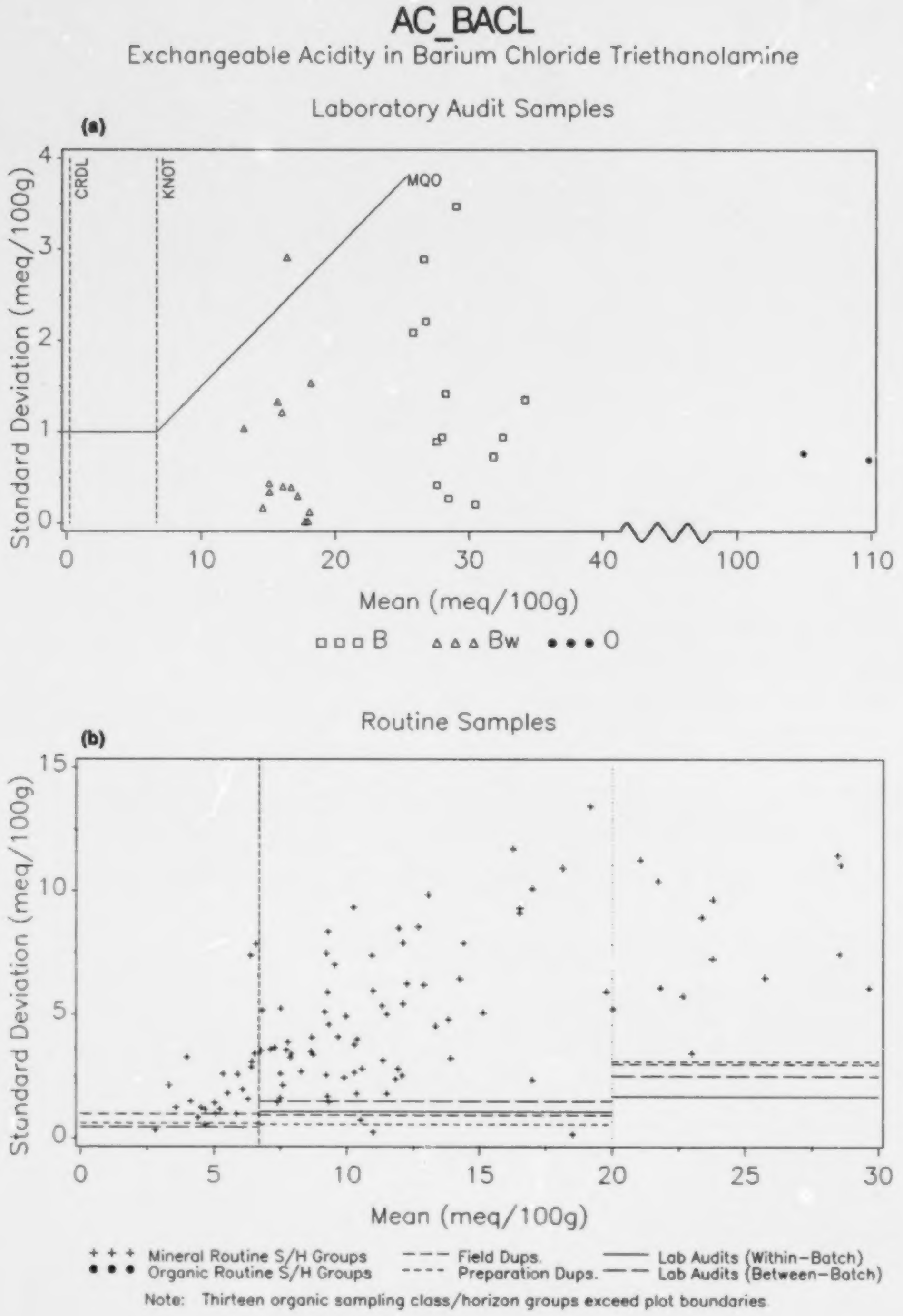


Figure 3-19. Range and frequency distribution of AC_BACL for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

Extractable Cations in Calcium Chloride

The analytical within-batch precision MQOs were satisfied for all six extractable cations in calcium chloride except for MG_CL2 data in the lower tier (see Table 3-7) which only slightly exceeded the objective. The effect of one inordinate audit sample pair out of 15 pairs within the tier was responsible for the failure to satisfy this MQO. The preparation and field within-batch MQOs were satisfied for all parameters in this group. The addition of a lower tier objective for the MASS extractable cation precision MQOs was helpful in evaluating the data compared to the earlier DDRP surveys. There was a general trend of increasing standard deviation with increased sources of confounded error.

Figures 3-20 through 3-25 are plots of laboratory audit sample data in relation to the within-batch MQOs and of the routine sample data in relation to selected QE samples. Supplemental information regarding uncertainty estimates is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

Table 3-7. Achievement of Measurement Quality Objectives for Within-Batch Precision of the Extractable Cations in Calcium Chloride

		Below the knot[c]					Above the knot[c]				
			SD	MQO	Pairs>MQO			RSD	MQO	Pairs>MQO	
Data set[a]	Parameter	df[b]	– meq/100g –		n	%	df	—— % ——		n	%
LAP	CA_CL2	27	0.0181	0.05	0	0.0	.	.	5	.	.
	MG_CL2	15	0.0058	0.005	1	6.7	12	3.6	10	0	0.0
	K_CL2	27	0.0013	0.005	0	0.0	.	.	10	.	.
	NA_CL2	25	0.0047	0.005	2	8.0	2	3.6	10	0	0.0
	FE_CL2	17	0.0007	0.01	0	0.0	.	.	15	.	.
	AL_CL2	27	0.0047	0.05	0	0.0	.	.	15	.	.
PD	CA_CL2	54	0.0146	0.05	1	1.9	.	.	8	.	.
	MG_CL2	37	0.0020	0.005	1	2.7	17	4.5	15	1	5.9
	K_CL2	53	0.0014	0.005	2	3.8	1	4.0	15	0	0.0
	NA_CL2	54	0.0009	0.005	0	0.0	.	.	15	.	.
	FE_CL2	25	0.0015	0.01	0	0.0	.	.	22	.	.
	AL_CL2	52	0.0047	0.05	0	0.0	.	.	22	.	.
FD	CA_CL2	27	0.0154	0.10	0	0.0	.	.	15	.	.
	MG_CL2	19	0.0048	0.01	1	5.3	8	7.8	30	0	0.0
	K_CL2	27	0.0028	0.01	0	0.0	.	.	30	.	.
	NA_CL2	27	0.0011	0.01	0	0.0	.	.	30	.	.
	FE_CL2	14	0.0012	0.02	0	0.0	.	.	45	.	.
	AL_CL2	26	0.0093	0.10	0	0.0	.	.	45	.	.
S/H	CA_CL2	618	0.0949				.	.			
	MG_CL2	209	0.0635				409	78.7			
	K_CL2	587	0.0197				31	125.4			
	NA_CL2	618	0.0097				.	.			
	FE_CL2	583	0.0098				22	228.0			
	AL_CL2	618	0.1042				.	.			

[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in meq/100g and percent, respectively, for mineral soil samples below and above the knot point of 1.0 meq/100g for CA, 0.05 meq/100g for MG, K, and NA, 0.07 meq/100g for FE, and 0.33 for AL; a dot signifies a lack of data occupying that range.

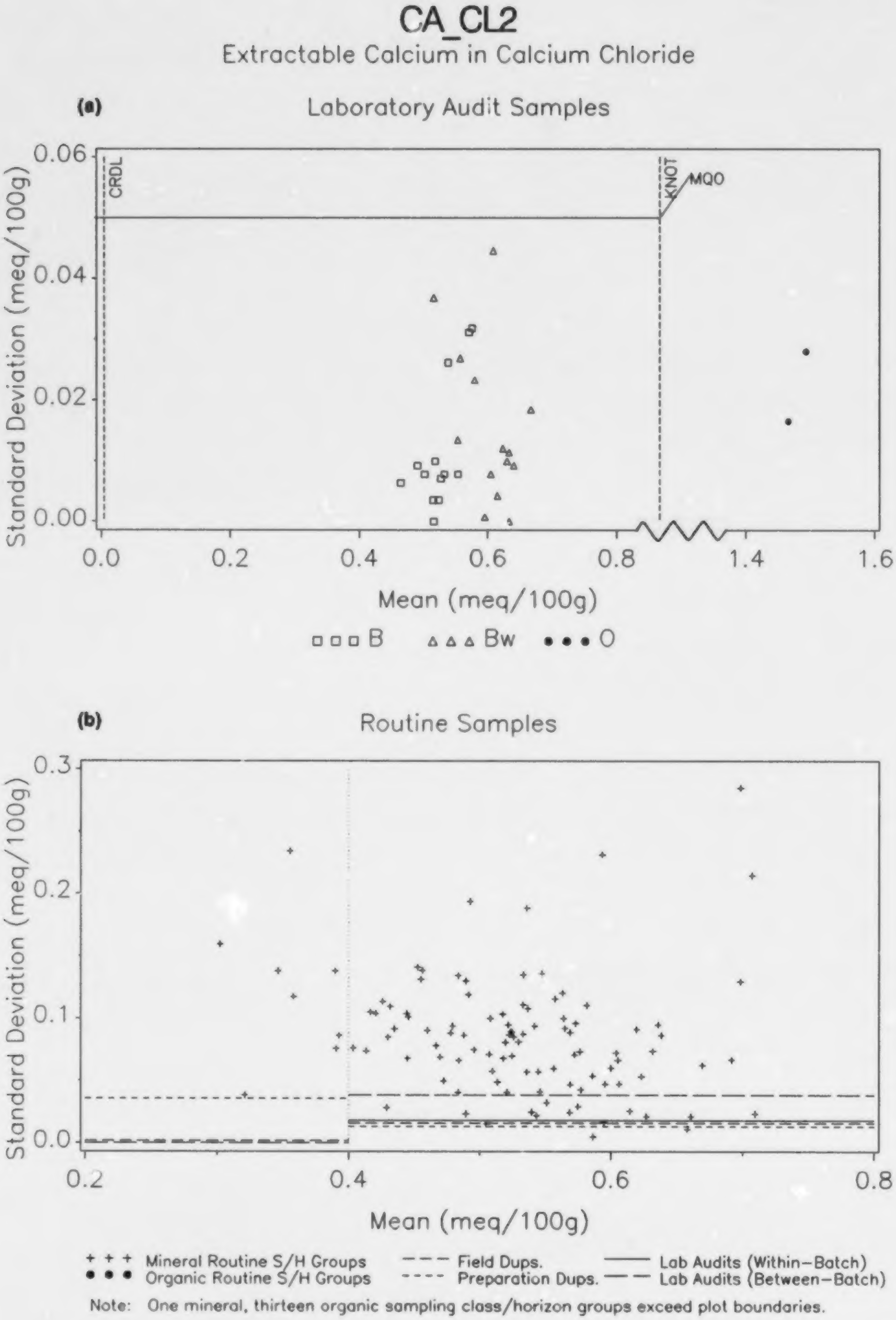
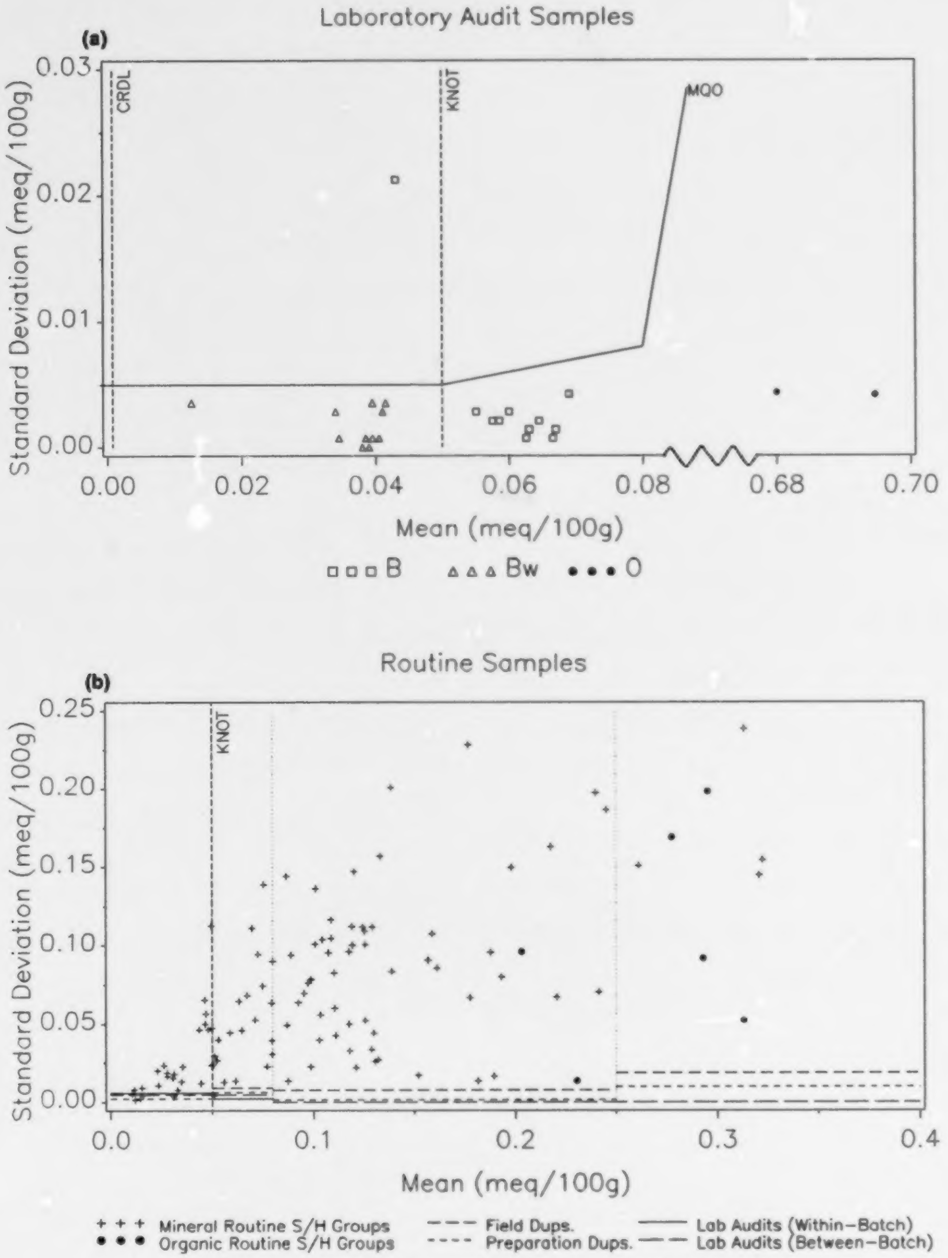


Figure 3-20. Range and frequency distribution of CA_CL2 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

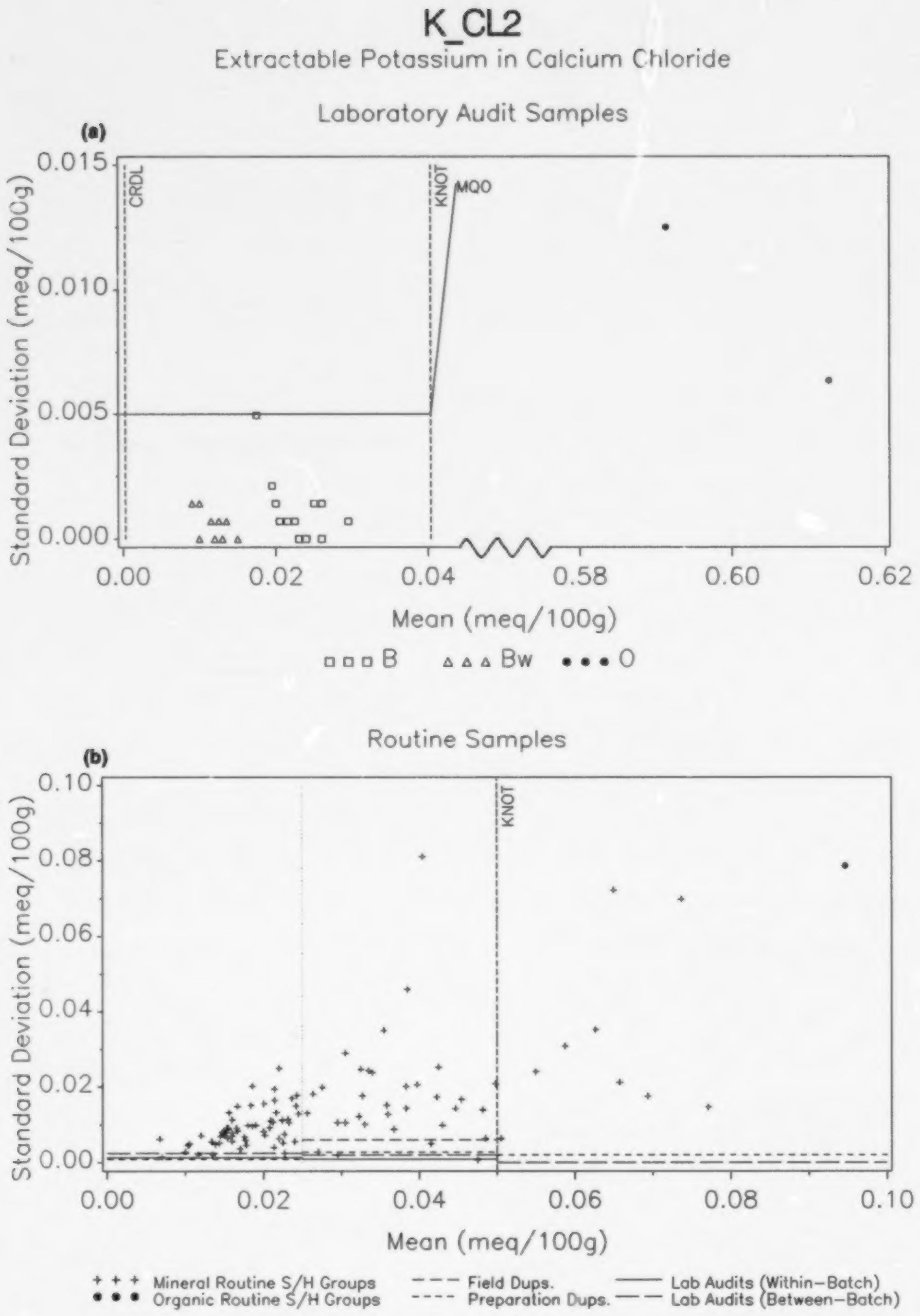
MG_CL2

Extractable Magnesium in Calcium Chloride



Note: Seven organic sampling class/horizon groups exceed plot boundaries.

Figure 3-21. Range and frequency distribution of MG_CL2 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: One mineral, twelve organic sampling class/horizon groups exceed plot boundaries.

Figure 3-22. Range and frequency distribution of K_CL2 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

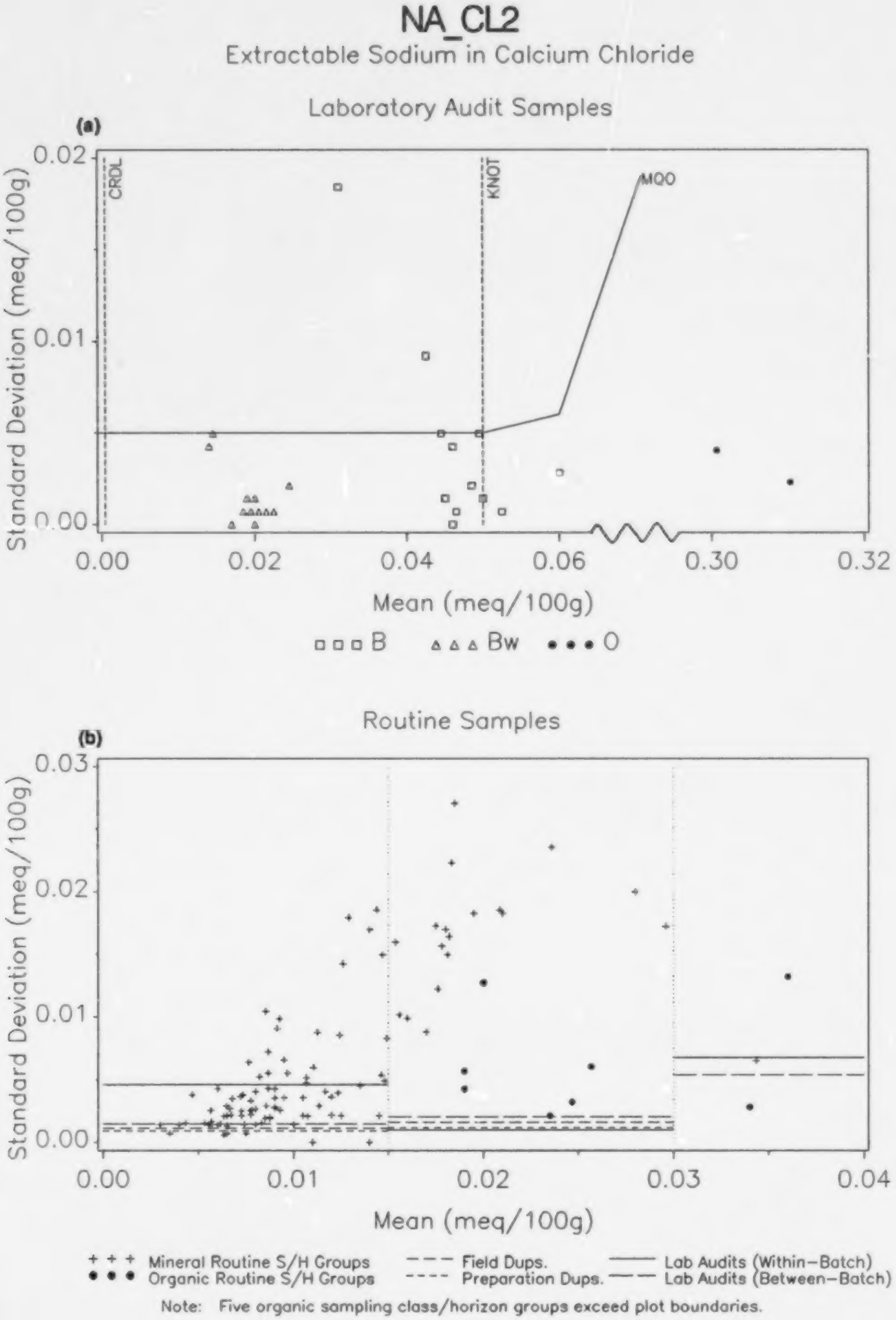
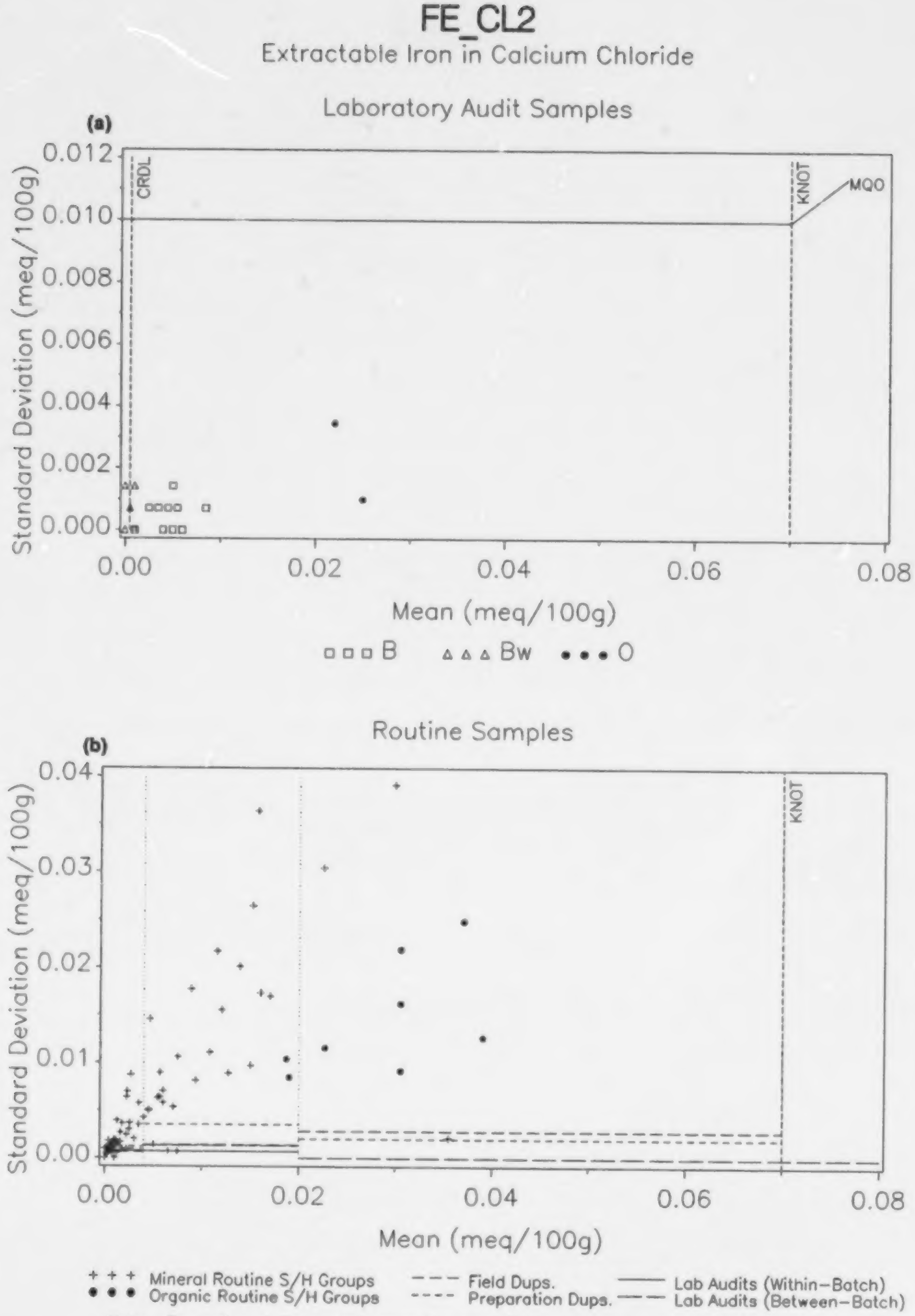


Figure 3-23. Range and frequency distribution of NA_CL2 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: Four mineral, five organic sampling class/horizon groups exceed plot boundaries.

Figure 3-24. Range and frequency distribution of FE_CL2 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

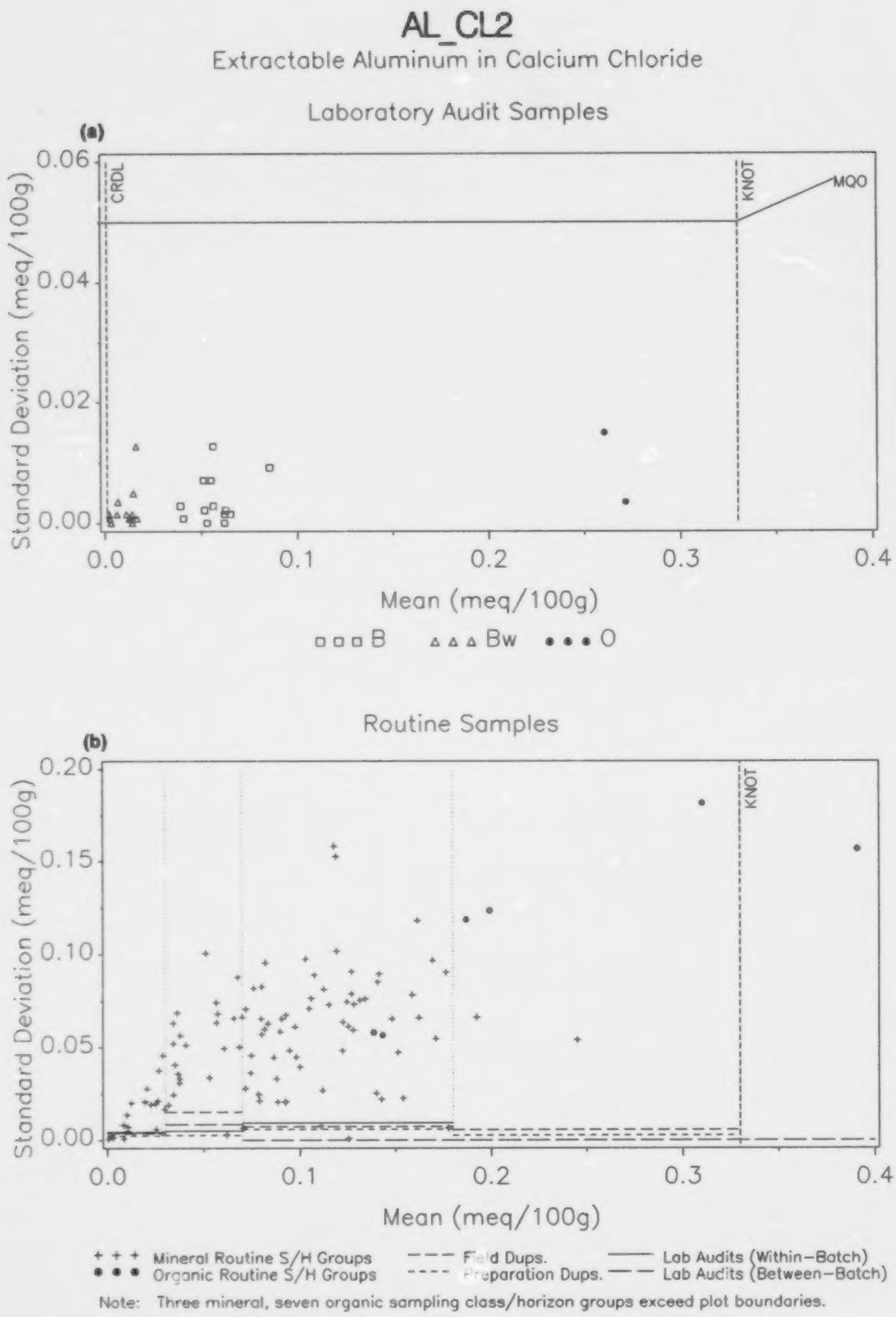


Figure 3-25. Range and frequency distribution of AL_CL2 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

Extractable Iron, Aluminum, and Silicon

The analytical within-batch precision MQOs for the extractable iron, aluminum, and silicon parameters were satisfied except for SI_AO above the knot (see Table 3-8). Extractable silicon was a new parameter that had not been measured in the previous DDRP surveys, and the laboratories apparently had difficulty in the analysis of SI_AO for upper tier precision. Unfortunately, there were no upper tier data for the preparation duplicates or field duplicates to confirm this hypothesis. Therefore, the QA staff has concluded that the upper tier analytical within-batch MQO of 10 percent RSD for this parameter might have been too restrictive for the laboratories to satisfy on a sustained basis. An MQO of 15 percent RSD or less may be a better expectation for the analytical within-batch precision, since it is thought that the possibility of incomplete extraction of silicon introduces more variability into the measurement of this cation than the other extractable cations.

The preparation and field within-batch MQOs were satisfied for all parameters in this group, except for the PD lower tier of FE_AO which only slightly exceeded the MQO. A general pattern of increasing standard deviation with increased sources of confounded error was maintained both below and above the knot.

Table 3-8. Achievement of Measurement Quality Objectives for Within-Batch Precision of Extractable Iron, Aluminum, and Silicon

Data set[a]	Parameter	Below the knot[c]					Above the knot[c]				
			SD	MQO	Pairs>MQO			RSD	MQO	Pairs>MQO	
		df[b]	— wt	% —	n	%	df	—— %	——	n	%
LAP	FE_PYP	.	.	0.03	.	.	27	3.4	10	0	0.0
	AL_PYP	.	.	0.03	.	.	27	5.5	10	1	3.7
	FE_AO	.	.	0.03	.	.	27	4.2	10	0	0.0
	AL_AO	.	.	0.03	.	.	27	4.9	10	1	3.7
	SI_AO	18	0.0154	0.03	1	5.6	9	12.0	10	3	33.3
	FE_CD	.	.	0.03	.	.	27	3.1	10	0	0.0
	AL_CD	.	.	0.03	.	.	27	6.7	10	2	7.4
PD	FE_PYP	32	0.0133	0.03	1	3.1	22	5.3	15	0	0.0
	AL_PYP	45	0.0151	0.03	3	6.7	9	5.0	15	0	0.0
	FE_AO	35	0.0361	0.03	2	5.7	19	5.8	15	0	0.0
	AL_AO	41	0.0189	0.03	1	2.4	13	5.7	15	1	7.7
	SI_AO	46	0.0111	0.03	1	2.2	.	.	15	.	.
	FE_CD	.	.	0.03	.	.	54	15.3	15	3	5.6
	AL_CD	37	0.0212	0.03	1	2.7	17	3.4	15	0	0.0
FD	FE_PYP	16	0.0213	0.06	0	0.0	11	6.1	30	0	0.0
	AL_PYP	22	0.0199	0.06	0	0.0	5	9.4	30	0	0.0
	FE_AO	18	0.0553	0.06	1	5.6	9	7.5	30	0	0.0
	AL_AO	20	0.0273	0.06	1	5.0	7	11.8	30	0	0.0
	SI_AO	23	0.0104	0.06	0	0.0	.	.	30	.	.
	FE_CD	.	.	0.06	.	.	27	6.4	30	0	0.0
	AL_CD	18	0.0175	0.06	0	0.0	9	3.7	30	0	0.0
S/H	FE_PYP	294	0.1869				324	81.1			
	AL_PYP	539	0.1384				79	111.1			
	FE_AO	286	0.2032				332	71.9			
	AL_AO	551	0.1152				67	61.4			
	SI_AO	614	0.0285				.	.			
	FE_CD	4	0.1347				614	44.9			
	AL_CD	437	0.1070				181	46.6			

[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

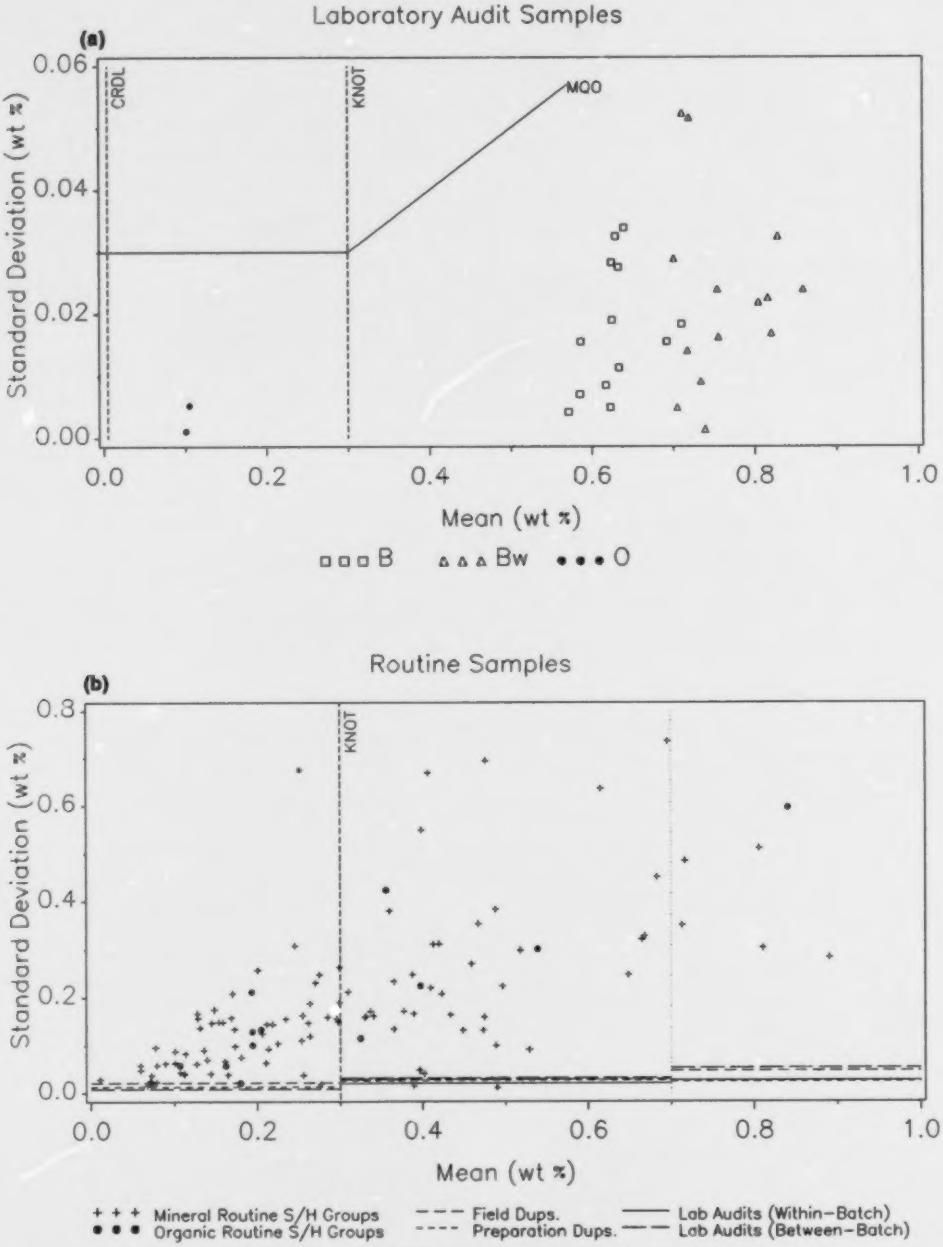
[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in weight percent and percent, respectively, for mineral soil samples below and above the knot point of 0.3 weight percent; a dot signifies a lack of data occupying that range.

Figures 3-26 through 3-32 are plots of the laboratory audit sample data in relation to the within-batch MQOs and of the routine sample data in relation to selected QE samples. Supplemental information regarding uncertainty estimates is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

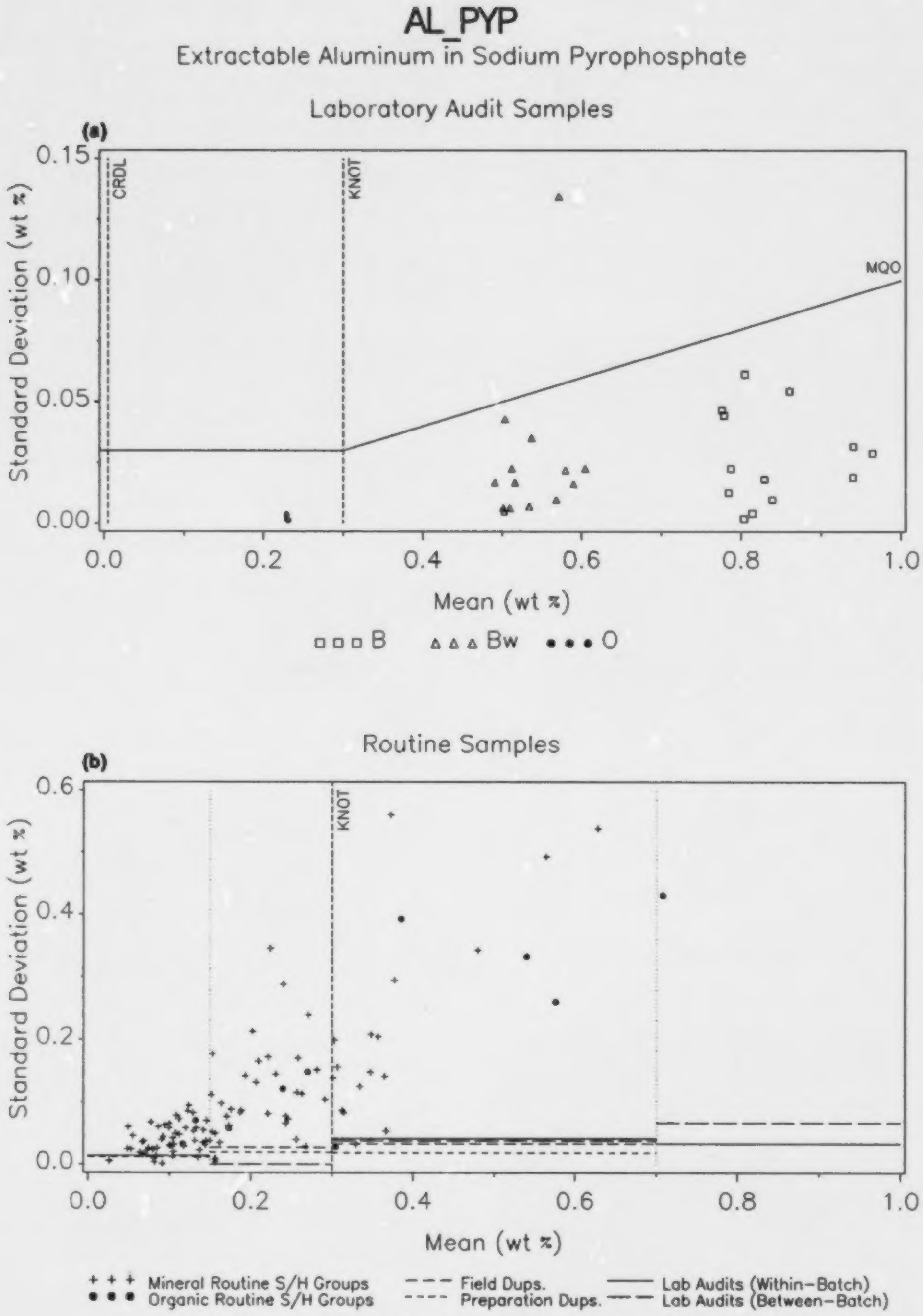
FE_PYP

Extractable Iron in Sodium Pyrophosphate



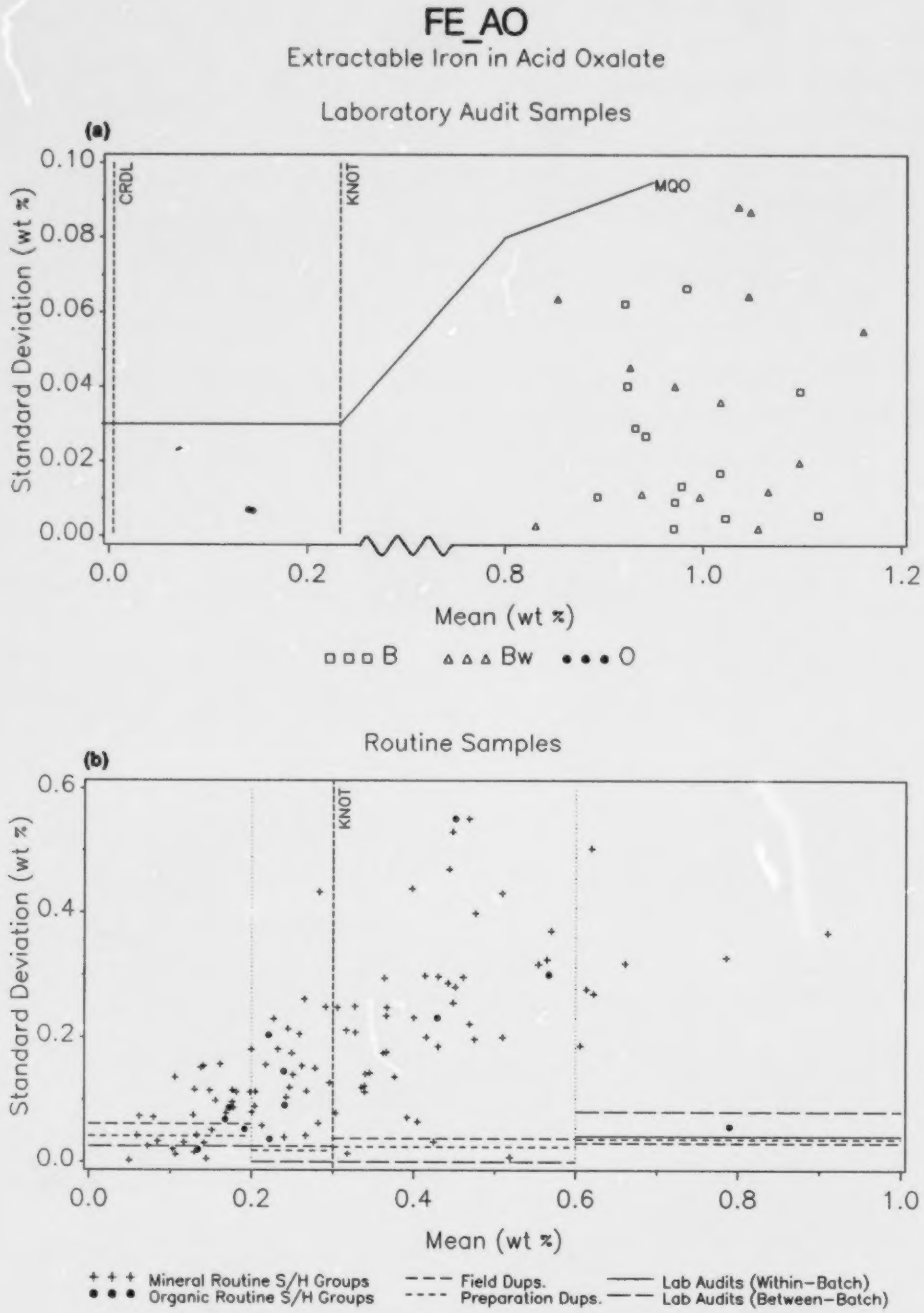
Note: Three mineral, one organic sampling class/horizon groups exceed plot boundaries.

Figure 3-26. Range and frequency distribution of FE_PYP for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine samole data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



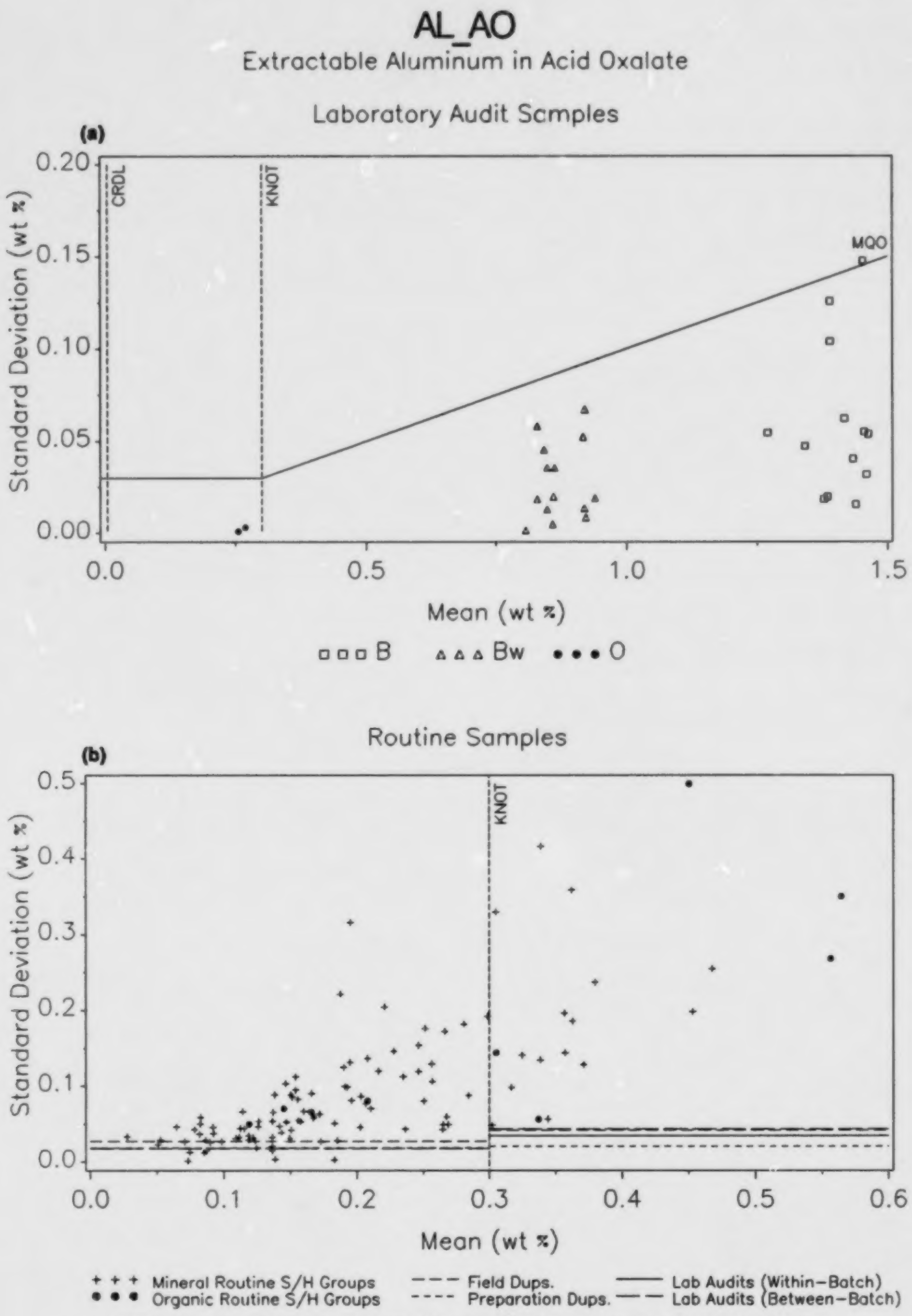
Note: Two mineral, three organic sampling class/horizon groups exceed plot boundaries.

Figure 3-27. Range and frequency distribution of AL_PYP for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



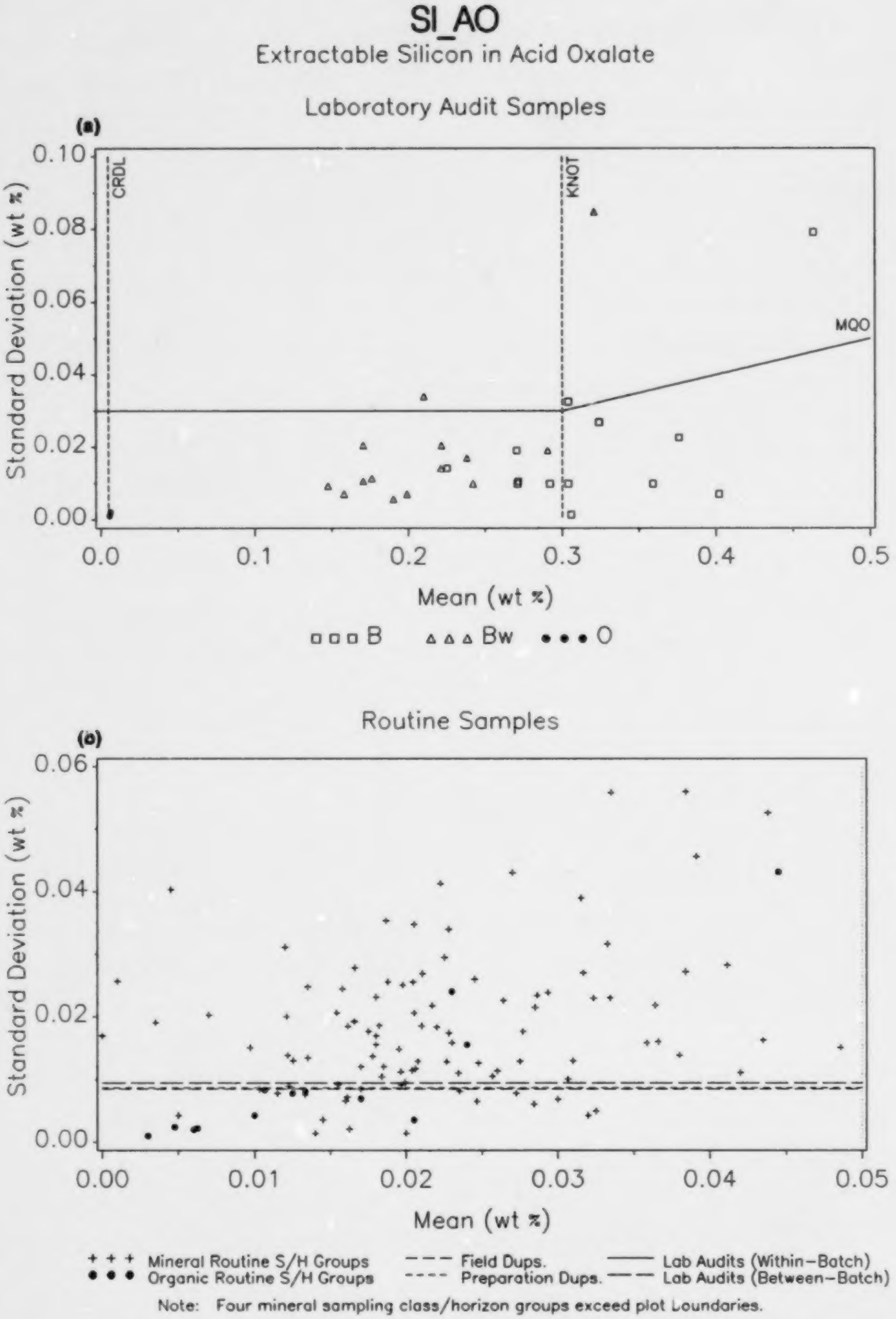
Note: Four mineral, one organic sampling class/horizon groups exceed plot boundaries.

Figure 3-28. Range and frequency distribution of FE_AO for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: One mineral, four organic sampling class/horizon groups exceed plot boundaries.

Figure 3-29. Range and frequency distribution of AL_AO for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



SI_AO

Extractable Silicon in Acid Oxalate

Laboratory Audit Samples

Routine Samples

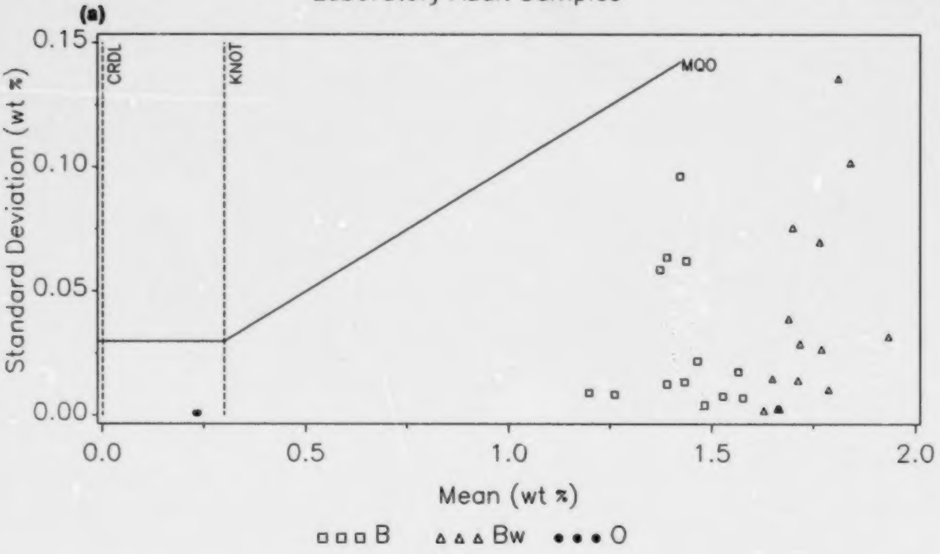
Note: Four mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-30. Range and frequency distribution of SI_AO for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

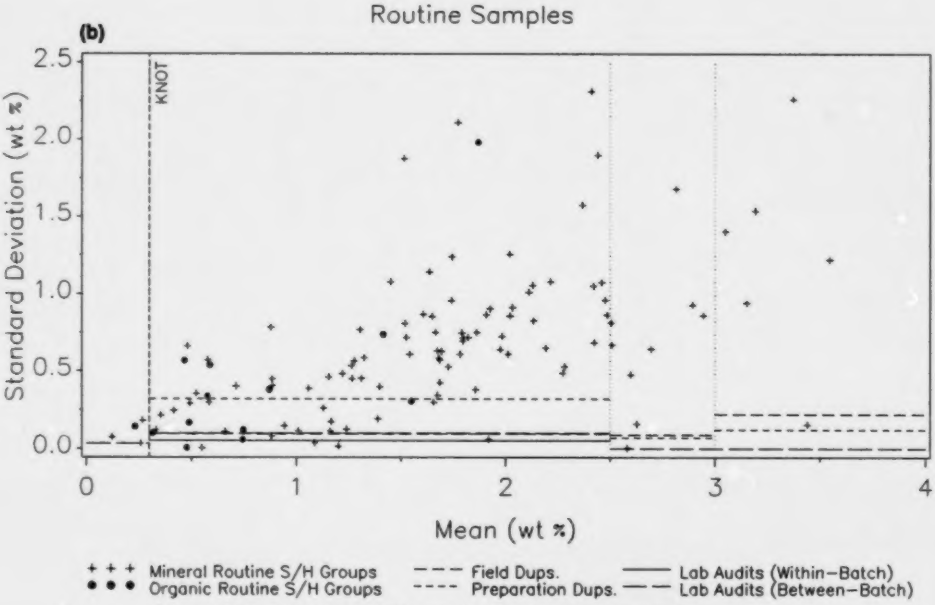
FE_CD

Extractable Iron in Citrate Dithionite

Laboratory Audit Samples



Routine Samples



Note: Three mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-31. Range and frequency distribution of FE_CD for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

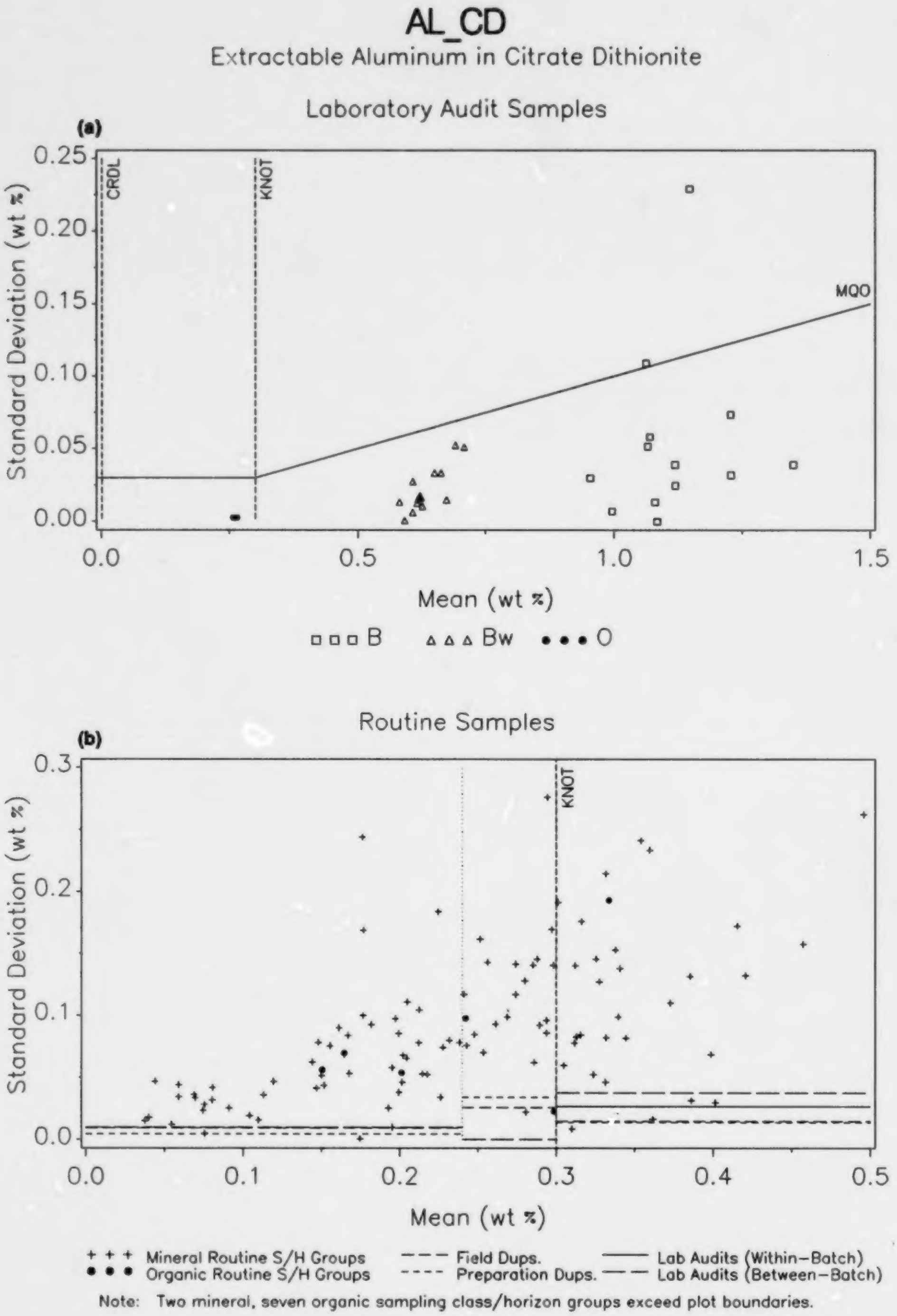


Figure 3-32. Range and frequency distribution of AL_CD for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

Extractable Sulfate and Sulfate Adsorption Isotherms

The analytical within-batch precision MQOs for the sulfate parameters were satisfied except for SO4_H2O, in which the lower tier MQO was slightly exceeded because of the inordinate effect of one laboratory audit sample pair (see Table 3-9). The analytical MQO for the SO4_0 parameter was satisfied, despite the fact that 46 percent of the individual audit sample pairs exceeded the MQO. This seems to have been a random error, however, because there was no evidence of high between-batch imprecision by a particular laboratory. Also, there was no pattern of this type seen in the preparation and field duplicate samples. The preparation and field within-batch MQOs were satisfied for all of the sulfate parameters.

There was a general trend of increasing standard deviation with increased sources of confounded error for the sulfate parameters.

Table 3-9. Achievement of Measurement Quality Objectives for Within-Batch Precision of Extractable Sulfate and Sulfate Adsorption Isotherms

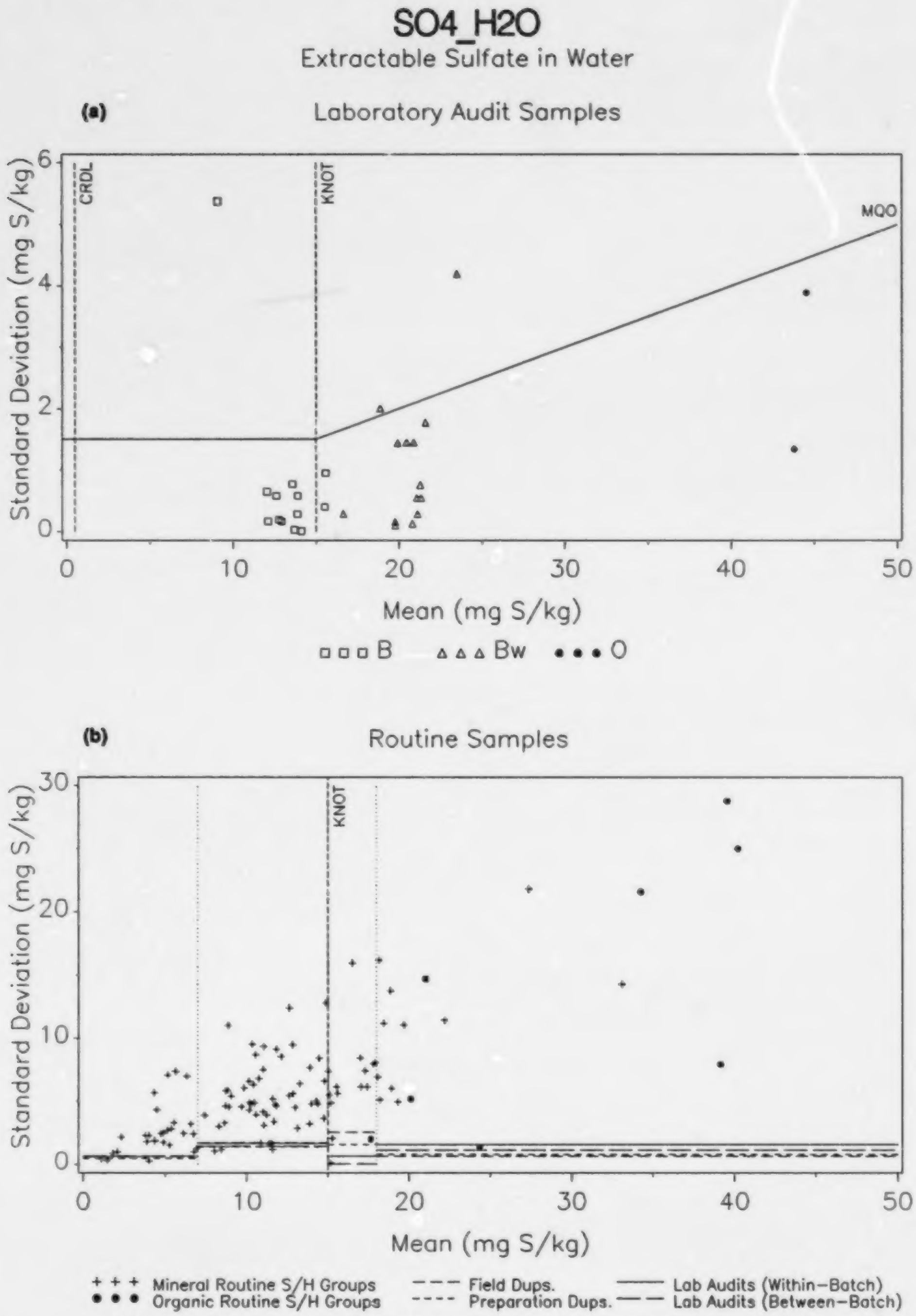
		Below the knot[c]					Above the knot[c]				
					Pairs>MQO			RSD	MQO	Pairs>MQO	
Data set[a]	Parameter	df[b]	SD	MQO	n	%	df	------ %	------	n	%
LAP	SO4_H2O	11	1.6719	1.50	1	9.1	16	7.3	10	2	12.5
	SO4_PO4	.	.	1.50	.	.	27	9.2	10	1	3.7
	SO4_0	14	0.0539	0.10	0	0.0	13	5.1	5	6	46.2
	SO4_2	1	0.0608	0.10	0	0.0	26	2.0	5	0	0.0
	SO4_4	.	.	0.10	.	.	27	2.9	5	3	11.1
	SO4_8	.	.	0.10	.	.	27	2.3	5	1	3.7
	SO4_16	.	.	0.10	.	.	27	2.6	5	1	3.7
	SO4_32	.	.	0.10	.	.	27	3.7	5	2	7.4
PD	SO4_H2O	34	1.3116	1.50	2	5.9	20	6.3	15	1	5.0
	SO4_PO4	2	1.4634	1.50	1	50.0	52	6.6	15	2	3.8
	SO4_0	41	0.0426	0.10	0	0.0	13	1.7	8	0	0.0
	SO4_2	12	0.0404	0.10	0	0.0	42	2.6	8	0	0.0
	SO4_4	.	.	0.10	.	.	54	2.5	8	1	1.9
	SO4_8	.	.	0.10	.	.	54	2.0	8	0	0.0
	SO4_16	.	.	0.10	.	.	54	1.8	8	1	1.9
	SO4_32	.	.	0.10	.	.	54	4.7	8	2	3.7
FD	SO4_H2O	19	1.6254	3.00	1	5.3	8	7.8	30	0	0.0
	SO4_PO4	1	2.5597	3.00	0	0.0	26	10.1	30	2	7.7
	SO4_0	21	0.1098	0.20	2	9.5	6	2.6	15	0	0.0
	SO4_2	7	0.0734	0.20	0	0.0	20	3.4	15	0	0.0
	SO4_4	.	.	0.20	.	.	27	4.3	15	0	0.0
	SO4_8	.	.	0.20	.	.	27	3.9	15	0	0.0
	SO4_16	.	.	0.20	.	.	27	2.7	15	0	0.0
	SO4_32	.	.	0.20	.	.	27	6.1	15	1	3.7
S/H	SO4_H2O	370	5.1195				248	278.6			
	SO4_PO4	49	4.6368				569	152.7			
	SO4_0	546	0.5822				72	287.5			
	SO4_2	78	0.7585				540	236.5			
	SO4_4	13	0.9980				605	175.9			
	SO4_8	1	0.6322				617	115.4			
	SO4_16	.	.				618	64.8			
	SO4_32	.	.				618	34.6			

[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in reporting units and percent, respectively, for mineral soil samples below and above the knot point of 15.0 mg S/kg for SO4_H2O and SO4_PO4 (2.0 mg S/L for SO4_0-32); a dot signifies a lack of data occupying that range.

Figures 3-33 through 3-40 are plots of the laboratory audit sample data in relation to the within-batch MQOs and of the routine sample data in relation to selected QE samples. Supplemental information regarding uncertainty estimates is presented in Appendix C and the identification of inordinate data values is presented in Appendix D.

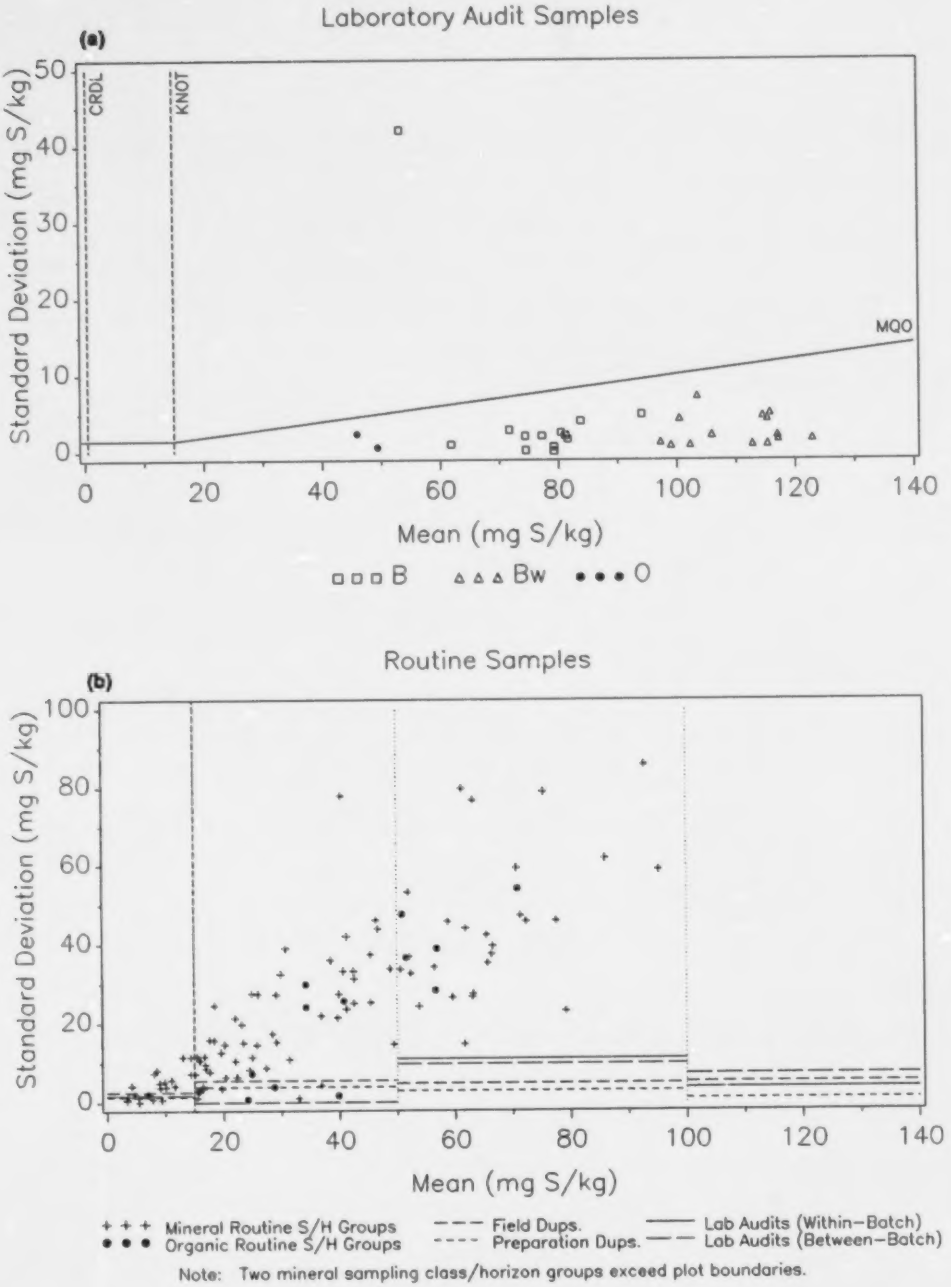


Note: One mineral, six organic sampling class/horizon groups exceed plot boundaries.

Figure 3-33. Range and frequency distribution of SO4_H20 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

SO4_PO4

Extractable Sulfate in Sodium Phosphate



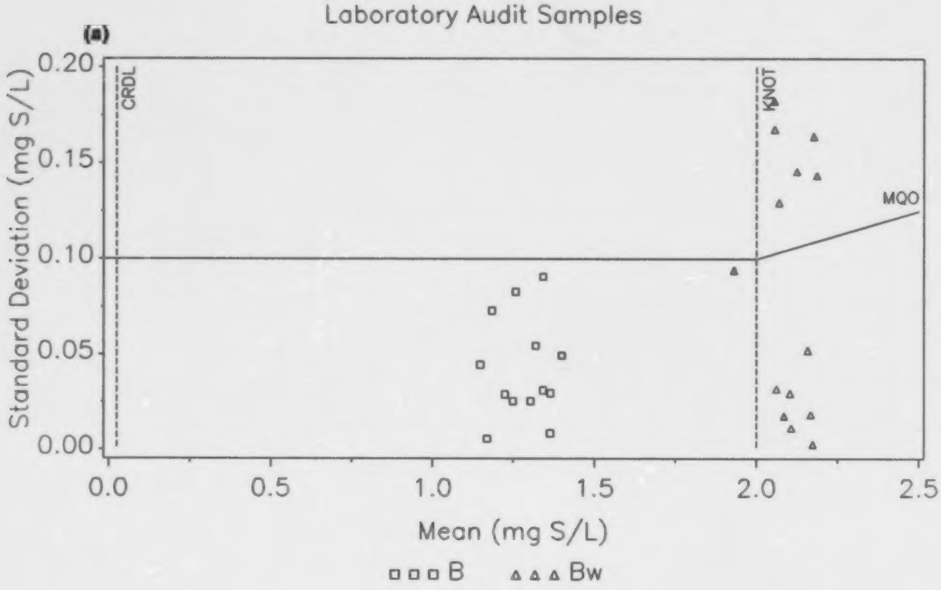
Note: Two mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-34. Range and frequency distribution of SO4_PO4 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

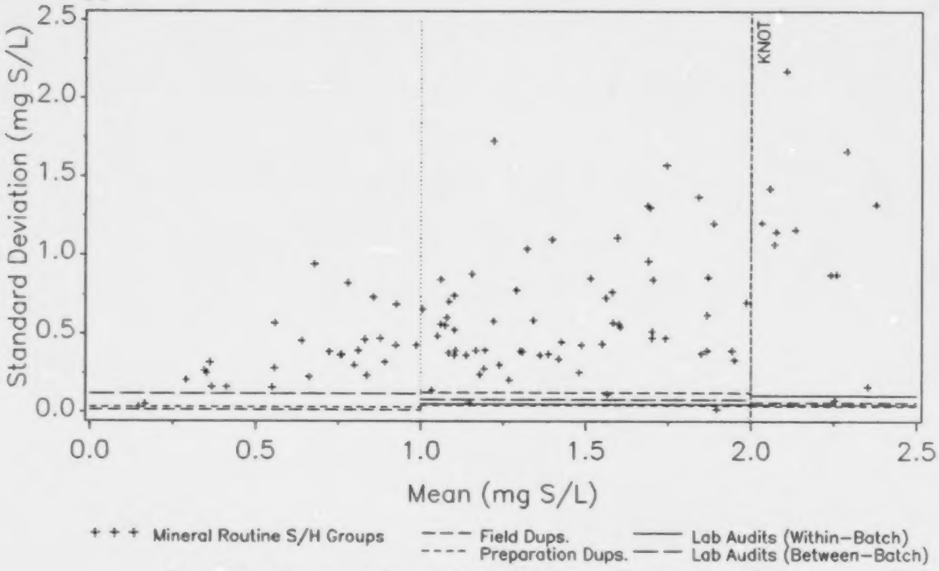
SO4_0

Sulfate Isotherm 0 mg S/L

Laboratory Audit Samples



Routine Samples



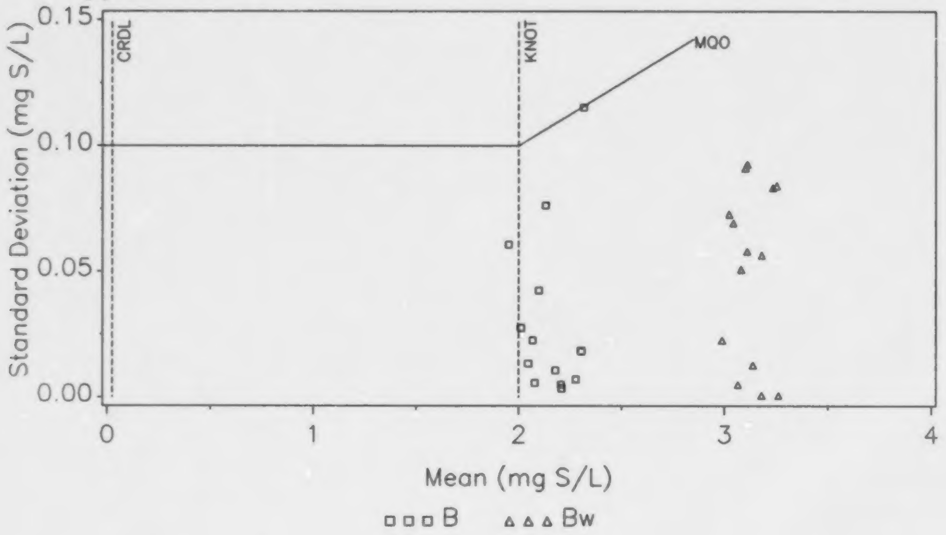
Note: Four mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-35. Range and frequency distribution of SO4_0 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

SO4_2

Sulfate Isotherm 2 mg S/L

Laboratory Audit Samples



Routine Samples

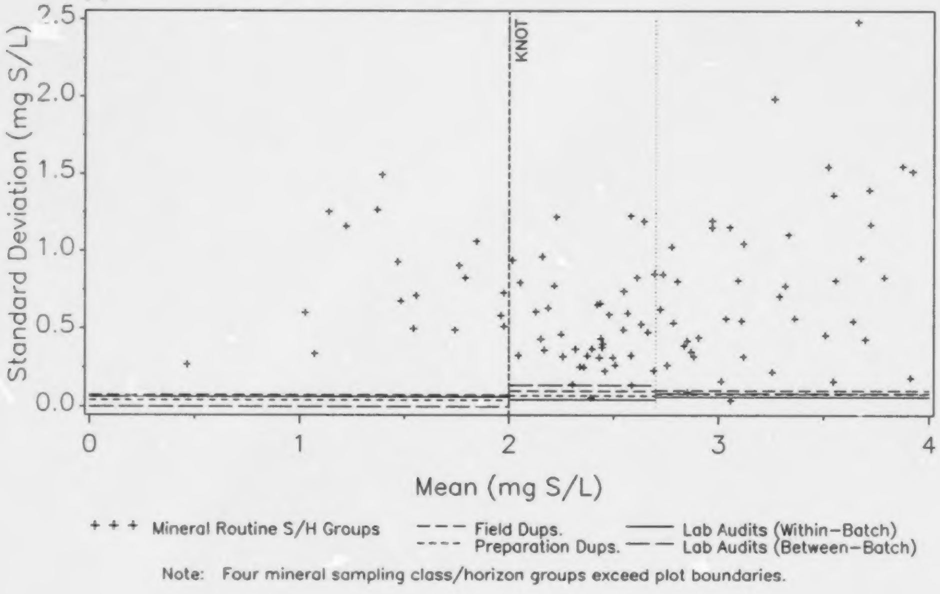
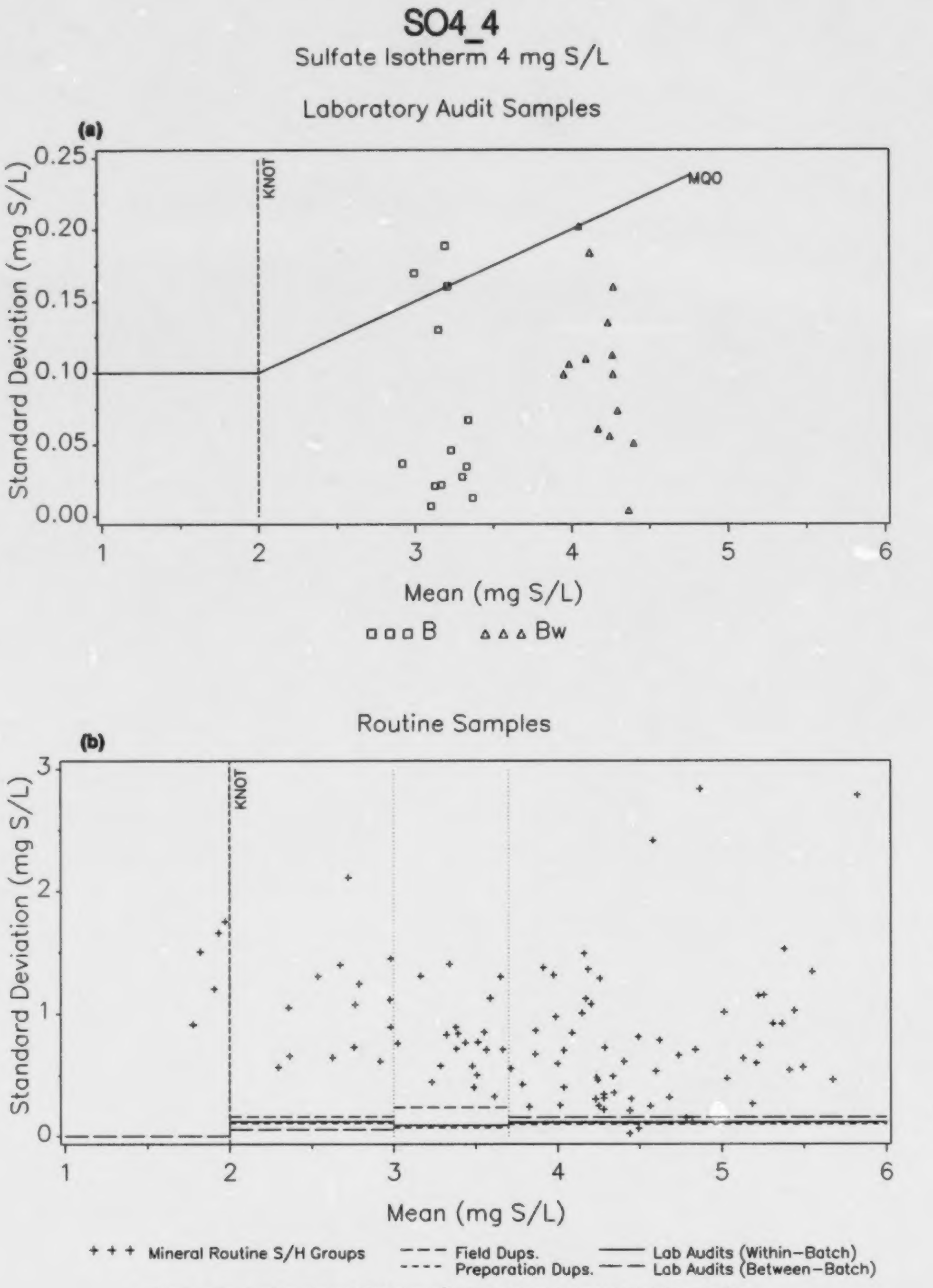
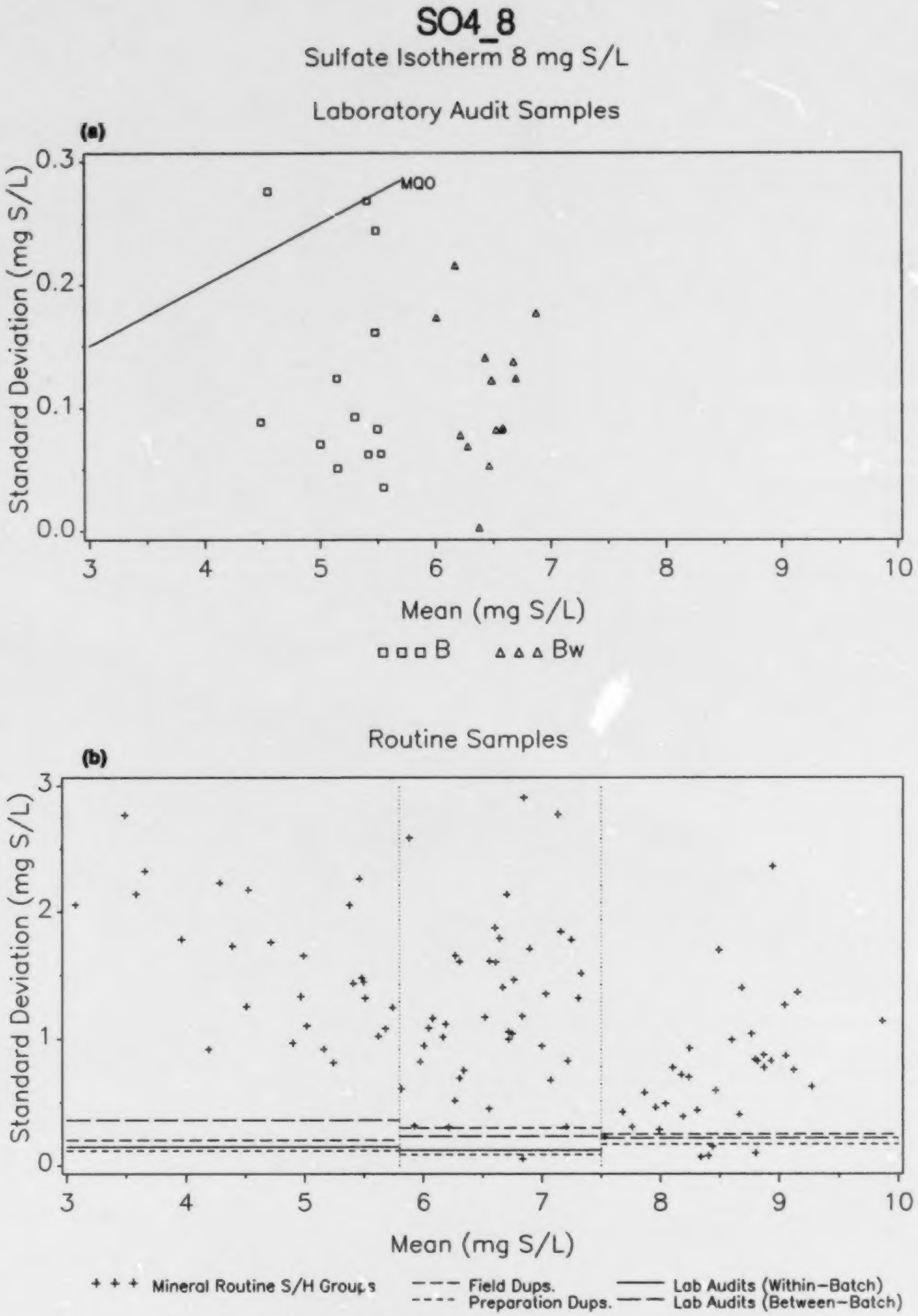


Figure 3-36. Range and frequency distribution of SO4_2 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: Four mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-37. Range and frequency distribution of SO4_4 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: Three mineral sampling class/horizon groups exceed plot boundaries.

Figure 3-38. Range and frequency distribution of SO4_8 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

SO4_16

Sulfate Isotherm 16 mg S/L

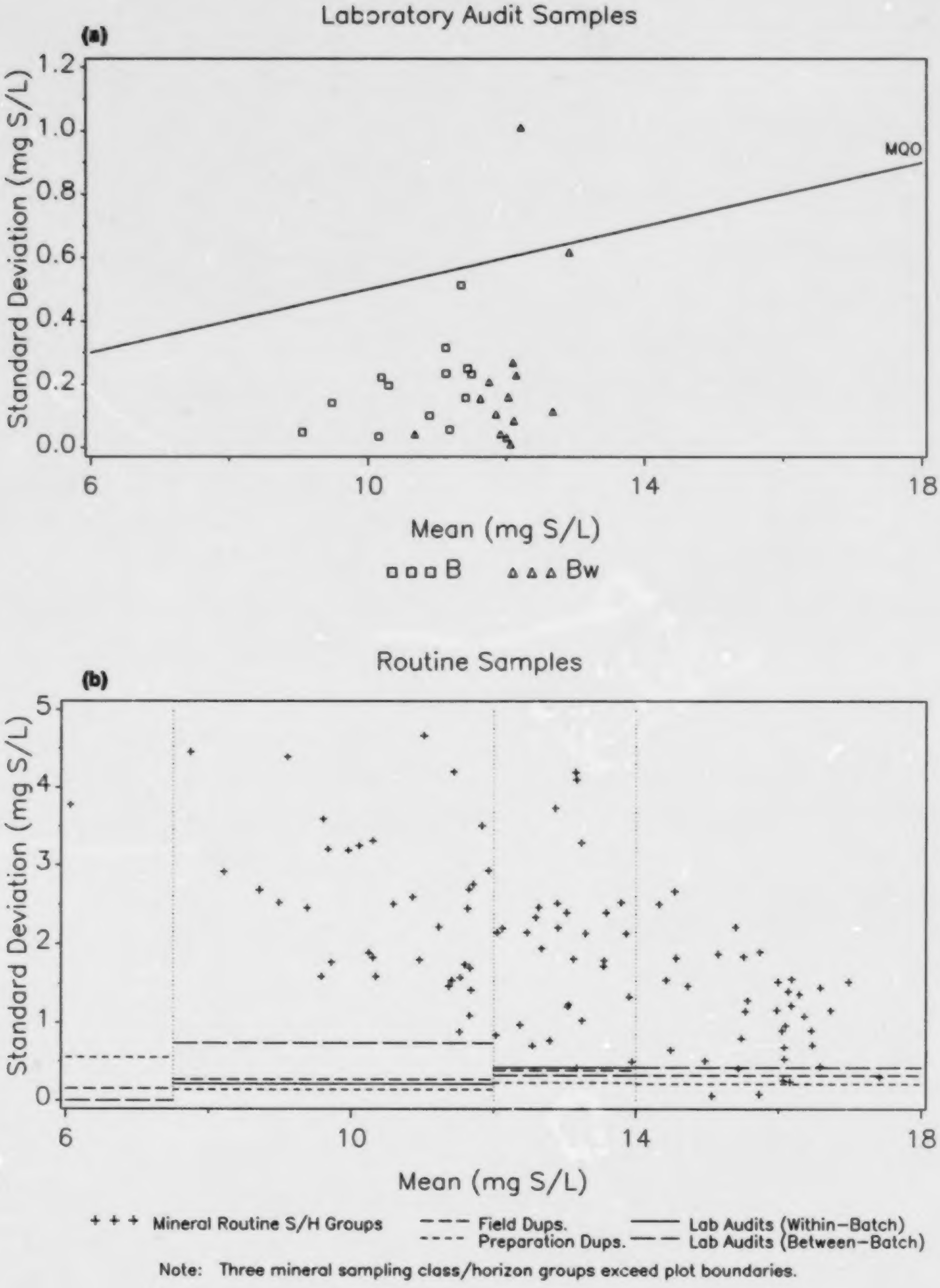


Figure 3-39. Range and frequency distribution of SO4_16 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

SO4_32

Sulfate Isotherm 32 mg S/L

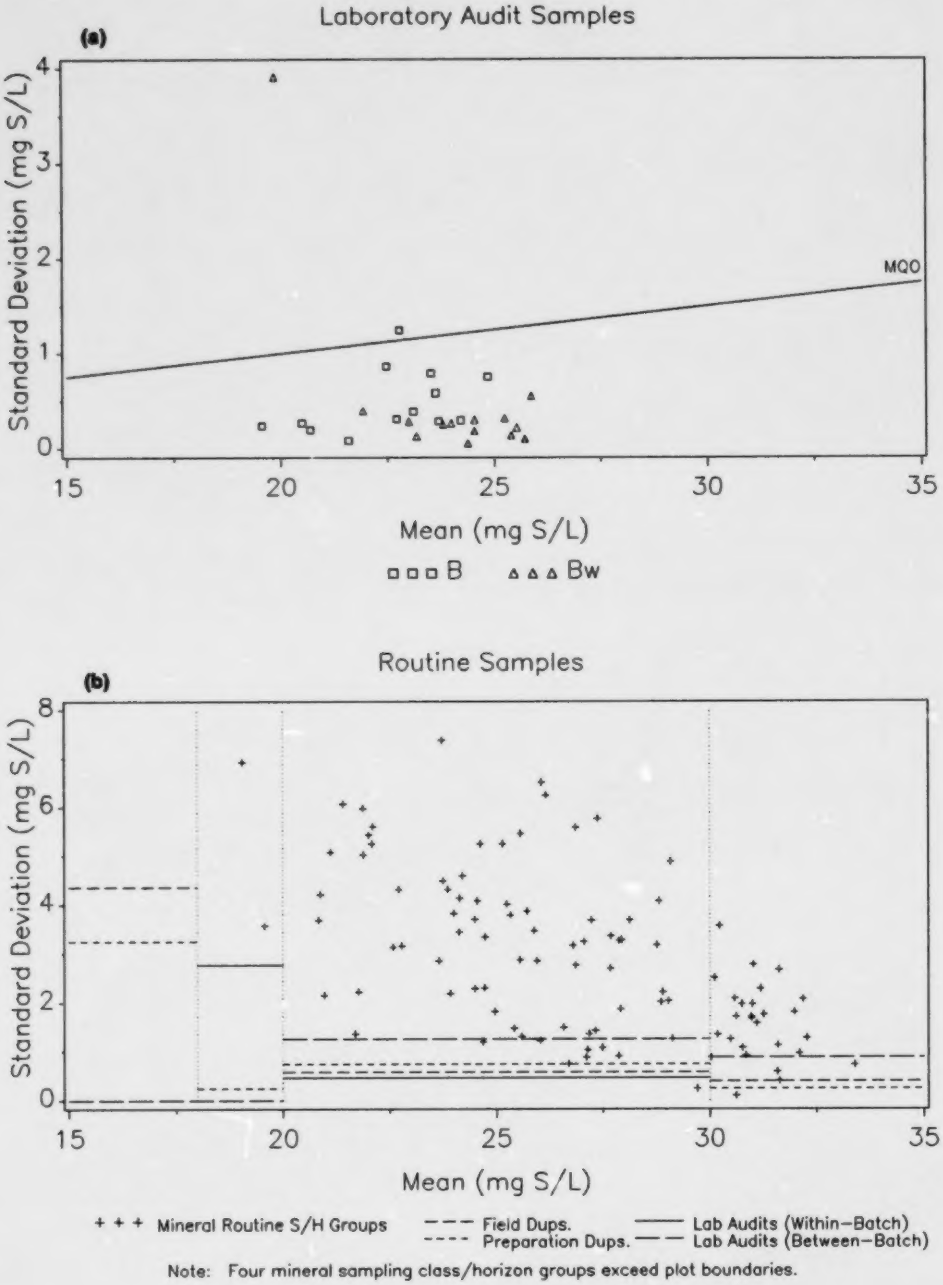


Figure 3-40. Range and frequency distribution of SO4_32 for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

Total Carbon, Nitrogen, and Sulfur

The analytical, preparation, and field within-batch precision MQOs were satisfied for total carbon, nitrogen, and sulfur (see Table 3-10). A general pattern of increasing standard deviation with increased sources of confounded error was maintained.

Figures 3-41 through 3-43 are plots of audit sample data in relation to the DQOs and routine sample data in relation to the QA samples. Supplemental information regarding uncertainty estimates is presented in Appendix C and the identification of inordinate values is presented in Appendix D.

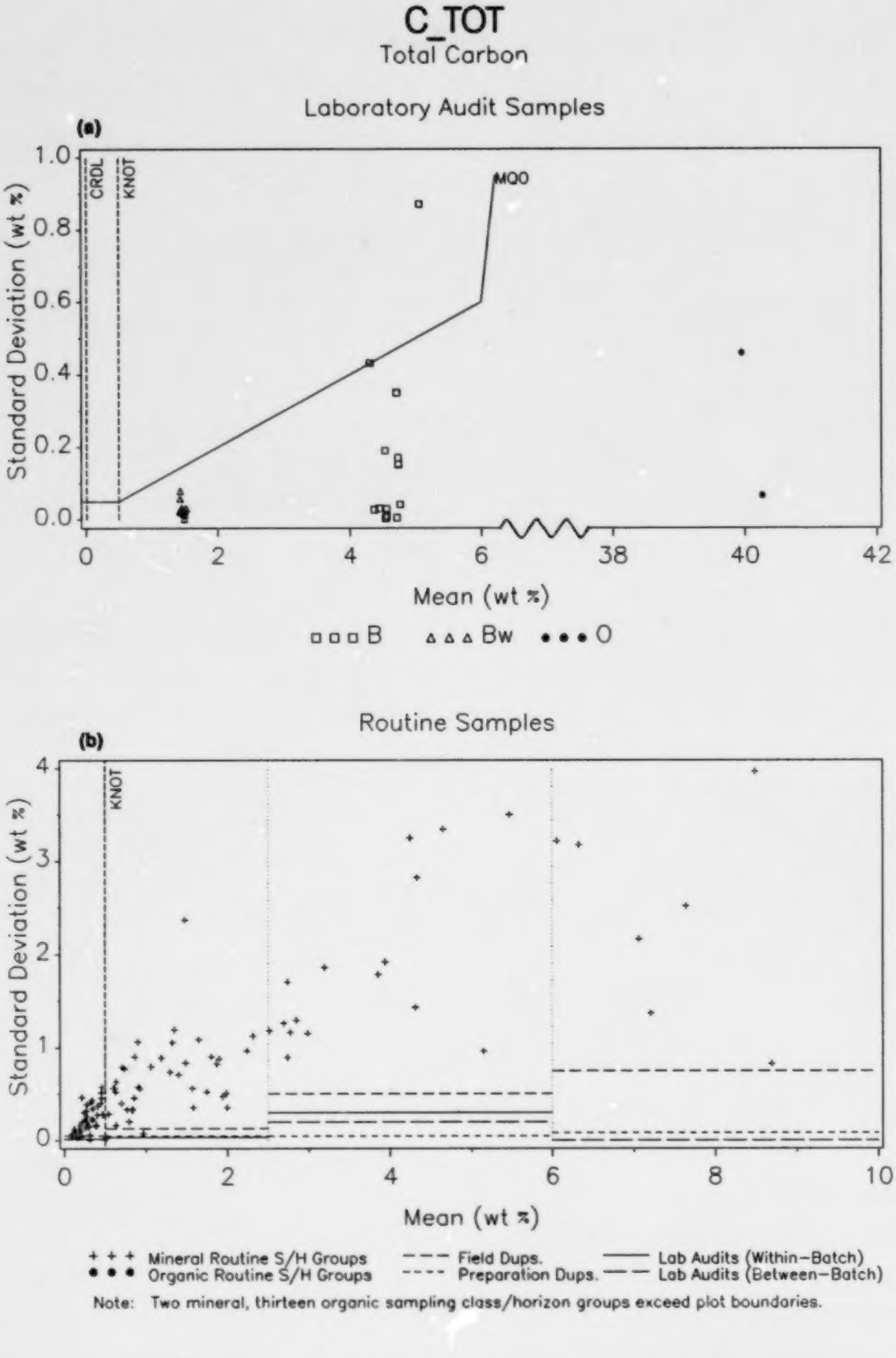
Table 3-10. Achievement of Measurement Quality Objectives for Within-Batch Precision of Total Carbon, Nitrogen, and Sulfur

		Below the knot[c]					Above the knot[c]				
			SD	MQO	Pairs>MQO			RSD	MQO	Pairs>MQO	
Data set[a]	Parameter	df[b]	— wt % —		n	%	df	—— % ——		n	%
LAP	C_TOT	.	.	0.05	.	.	27	7.0	10	2	7.4
	N_TOT	14	0.0053	0.015	1	7.1	13	3.8	10	0	0.0
	S_TOT	5	0.0011	0.002	0	0.0	22	7.8	10	1	4.5
PD	C_TOT	28	0.0119	0.05	0	0.0	26	3.0	15	1	3.8
	N_TOT	50	0.0039	0.015	0	0.0	4	1.6	15	0	0.0
	S_TOT	46	0.0008	0.002	2	4.3	8	2.2	15	0	0.0
FD	C_TOT	13	0.0502	0.10	1	7.7	14	17.0	30	1	7.1
	N_TOT	25	0.0053	0.03	0	0.0	2	7.7	30	0	0.0
	S_TOT	23	0.0011	0.004	0	0.0	4	8.4	30	0	0.0
S/H	C_TOT	279	0.3334				339	127.5			
	N_TOT	526	0.0342				92	56.9			
	S_TOT	527	0.0070				91	259.8			

[a] LAP = Laboratory audit pairs; PD = Preparation duplicates; FD = Field duplicates; S/H = Sampling class/horizon routine samples.

[b] Degrees of freedom.

[c] Standard deviations and relative standard deviations expressed in weight percent and percent, respectively, for mineral soil samples below and above the knot point of 0.5 weight percent for C_TOT, 0.15 weight percent for N_TOT, and 0.02 weight percent for S_TOT; a dot signifies a lack of data occupying that range.



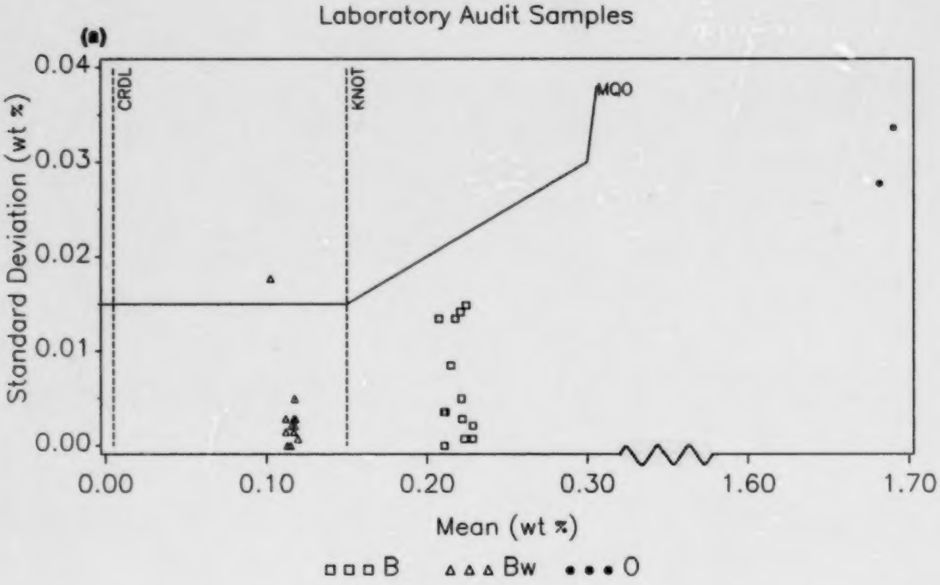
Note: Two mineral, thirteen organic sampling class/horizon groups exceed plot boundaries.

Figure 3-41. Range and frequency distribution of C_TOT for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

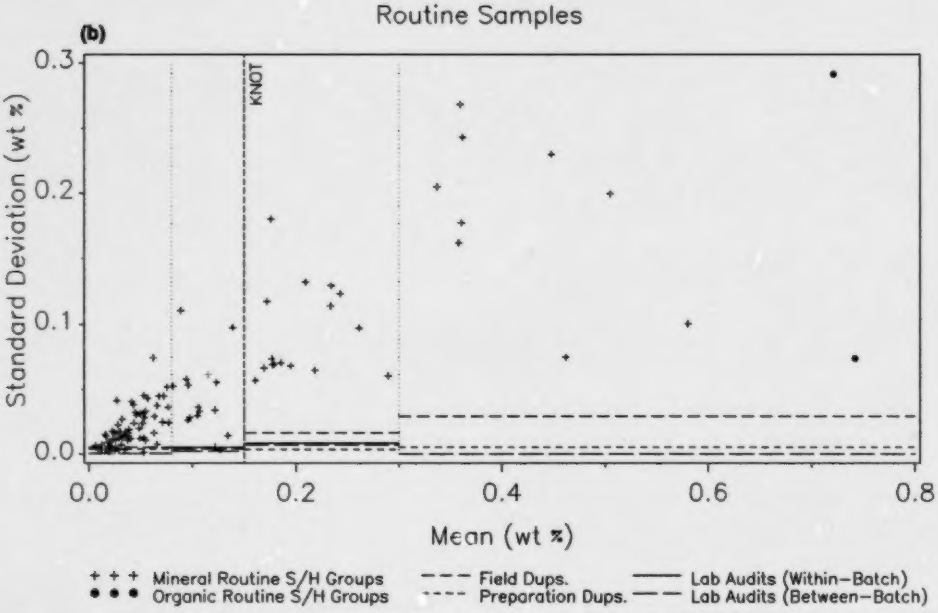
N_TOT

Total Nitrogen

Laboratory Audit Samples



Routine Samples

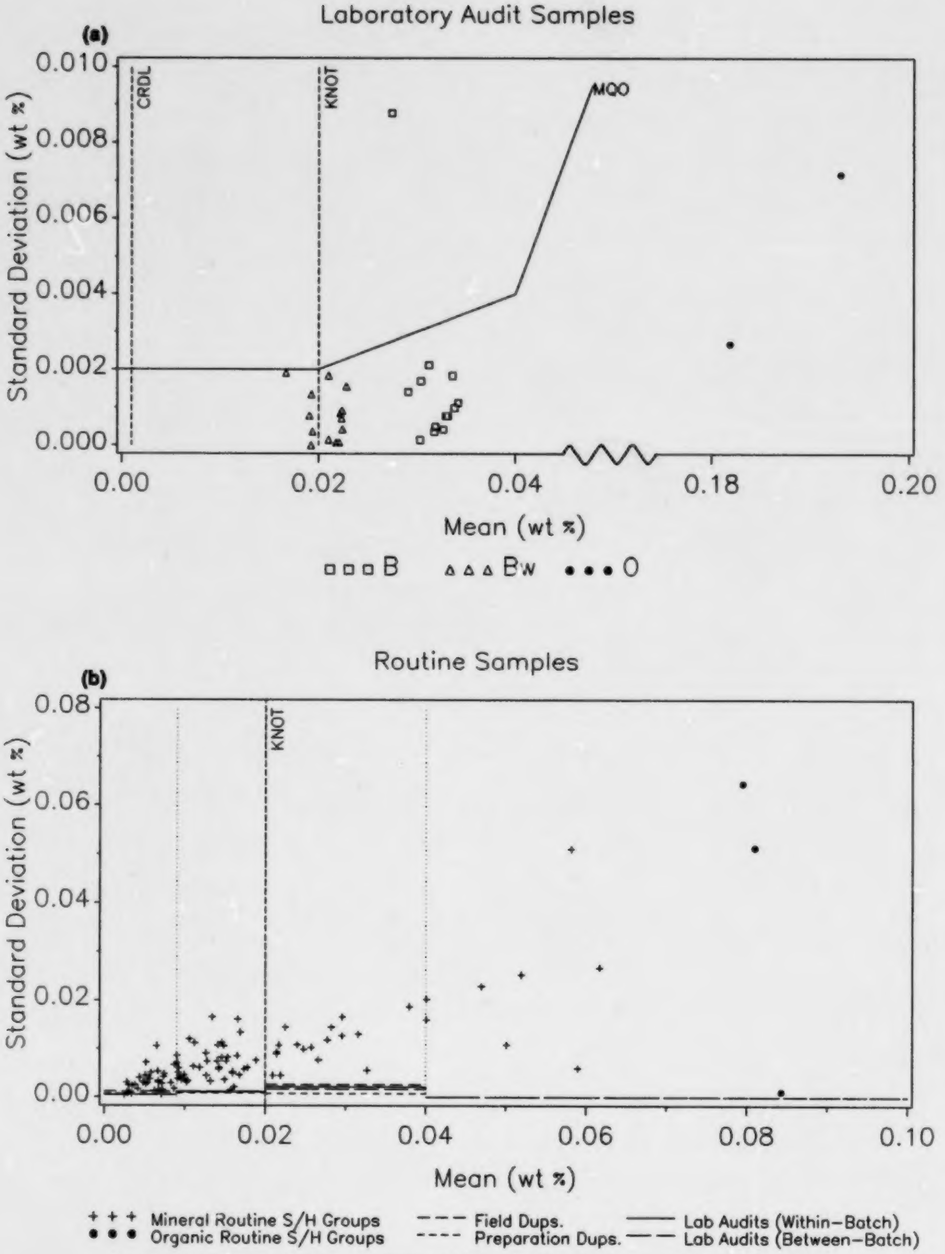


Note: Eleven organic sampling class/horizon groups exceed plot boundaries.

Figure 3-42. Range and frequency distribution of N_TOT for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

S_TOT

Total Sulfur



Note: One mineral, ten organic sampling class/horizon groups exceed plot boundaries.

Figure 3-43. Range and frequency distribution of S_TOT for: (a) laboratory audit samples and their relation to the analytical within-batch precision measurement quality objective (MQO) and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

Assessment of Accuracy

The accuracy considerations of importance to the MASS were investigated using data primarily derived from the laboratory audit samples, as described in the following subsections.

Bias

The B and Bw horizon LAP samples and the C horizon LAL samples were used to estimate analytical bias, and the corresponding FAP and FAL samples were used to estimate system-wide bias. It was found that the field and preparation components of system-wide bias were negligible and that bias was principally an analytical laboratory component. Table 3-11 shows the analytical bias values expressed in reporting units for the mineral soil audit samples. Bias was not determined for the organic audit samples because the low number of organic batches analyzed resulted in insufficient degrees of freedom for meaningful statistical analysis.

Analytical bias was negligible when compared with the SDLs of all 37 parameters for which detection limits were established. This comparison could not be made for the 13 physical and pH parameters. For CEC_OAC, bias exceeded the SDL for Laboratories 1 and 2 which titrated the samples, but bias was negligible for Laboratory 4 which used flow injection analysis. Bias for the two newly-established parameters for the MASS, i.e., AL_CL and SI_AO, were both much less than their respective SDLs. The majority of the analytical bias estimates for the parameters were on the positive, or high, side of the reference value.

As was previously stated, none of the audit samples were assigned a single reference value for contractual compliance purposes. Instead, each audit sample was assigned a range of acceptable reference values in accuracy windows derived from confidence intervals constructed around mean values established from previous DDRP laboratory analyses. This approach was taken for the purpose of monitoring the laboratories to ensure acceptable data on a batch-by-batch basis for the duration of the survey. In this framework, bias within the windows was acceptable and allowable for each parameter

Table 3-11. Analytical Bias Estimates

Parameter	Reporting units	Analytical bias
SAND	wt %	0.3211
VCOS	"	0.3948
COS	"	0.7606
MS	"	0.5632
FS	"	-0.5363
VFS	"	-0.8188
SILT	"	0.9283
COSI	"	0.2344
FSI	"	0.2929
CLAY	"	-0.6168
PH_H20	pH units	-0.0319
PH_002M	"	0.0277
PH_01M	"	-0.0216
CA_CL	meq/100g	-0.0028
MG_CL	"	0.0011
K_CL	"	0.0010
NA_CL	"	-0.0013
AL_CL	"	-0.0615[a]
CA_OAC	meq/100g	0.0005
MG_OAC	"	0.0007
K_OAC	"	0.0059
NA_OAC	"	0.0044
CEC_CL[c]	meq/100g	-0.0261
CEC_CL[d]	meq/100g	0.0217
CEC_OAC[c]	"	-0.6132*
CEC_OAC[d]	"	0.0523
AC_BACL	"	-0.1611
CA_CL2	meq/100g	0.0248
MG_CL2	"	0.0024
K_CL2	"	0.0005
NA_CL2	"	0.0012
FE_CL2	"	-0.0004
AL_CL2	"	0.0023
FE_PYP	wt %	-0.0183
AL_PYP	"	-0.0043
FE_AO	"	0.0099
AL_AO	"	0.0009
SI_AO	"	-0.0034[a]
FE_CD	"	0.0136
AL_CD	"	0.0030
SO4_H2O	mg S/kg	0.1055
SO4_PO4	"	2.0341
SO4_0	mg S/L	0.0358
SO4_2	"	0.0446
SO4_4	"	0.0526
SO4_8	"	0.0546
SO4_16	"	0.1053
SO4_32	"	0.1026
C_TOT[b]	wt %	-0.0352
N_TOT[b]	"	0.0016
S_TOT[b]	"	-0.0007

[a] Based on data from B horizon FAP samples only.
[b] Analyzed by Laboratory 2 only.
[c] Analysis by titration (Laboratories 1 and 2).
[d] Analysis by FIA (Laboratory 4 only).
* Exceeds the system detection limit (SDL).

from a contractual standpoint. The estimation of bias at the completion of the survey, however, included this within-window uncertainty in the calculations of bias.

For assessment purposes, it was important to evaluate the occurrences which were outside the upper and lower limits of the windows, and to identify their contribution to the bias estimates for each parameter across audit samples. Table 3-12 shows the percentage of observations that were outside the respective accuracy windows and the magnitude of their contribution to the analytical bias estimates given previously in Table 3-11. The results show a very wide range in the ratios of bias for values outside the window compared to the total analytical bias. Except for S_TOT, every parameter had fewer than 20 percent of its values outside the accuracy window. A high second value in the ratio implies a lower contribution to the bias. Parameters that had a high percentage of observations outside the window and ratios from 1:1 to 1:3 generally had values at varying distances from the window, while those parameters that had a low percentage of observations outside the window and the same low ratios generally had only extreme values outside the window.

Generally, the contribution of outside-window values to the analytical bias is low. Only 11 of the 50 parameters had values outside the window that contributed more than one-third to the bias: COSI, FSI, MG_CL, AL_CL, MG_OAC, CEC_CL, AL_PYP, FE_AO, SI_AO, AL_CD, and S04_32. Although the percentage of samples outside the window for S_TOT is high, the contribution to overall bias was relatively low.

Laboratory Differences

The laboratory differences, identified through a series of assessments of laboratory means across audit samples in relation to the reference values, are described in the following subsections.

Table 3-13 shows the percent differences, averaged across the B, Bw, and C horizon laboratory audit samples, of the laboratory mean values from the pooled reference value for each parameter. Differences were not determined for the organic samples because

Table 3-12. Contribution of Outlying Audit Samples to Overall Analytical Bias

Parameter	Laboratory audit samples exceeding window boundaries: Percent[a]	Ratio[b]
SAND	3.7	1 : 17
VCOS	18.5	1 : 18
COS	6.2	1 : 12
MS	17.3	1 : 6
FS	8.6	1 : 6
VFS	2.5	1 : 47
SILT	12.3	1 : 5
COSI	6.2	1 : 1
FSI	12.3	1 : 1
CLAY	13.6	1 : 68
PH_H2O	6.2	1 : 46
PH_002M	7.4	1 : 4
PH_01M	2.5	1 : 54
CA_CL	6.2	1 : 3
MG_CL	6.2	1 : 1
K_CL	1.2	1 : 10
NA_CL	2.5	1 : 4
AL_CL	3.0	1 : 1
CA_OAC	7.4	1 : 3
MG_OAC	3.7	1 : 1
K_OAC	14.8	1 : 10
NA_OAC	3.7	1 : 22
CEC_CL	6.2	1 : 1
CEC_OAC	1.2	1 : 44
AC_BACL	11.1	1 : 4
CA_CL2	1.2	1 : 100
MG_CL2	17.3	1 : 24
K_CL2	3.7	1 : 5
NA_CL2	13.5	1 : 6
FE_CL2	8.6	1 : 4
AL_CL2	6.2	1 : 8
FE_PYP	8.6	1 : 100
AL_PYP	16.0	1 : 1
FE_AO	17.3	1 : 2
AL_AO	0.0	–
SI_AO	4.0	1 : 2
FE_CD	9.9	1 : 4
AL_CD	4.9	1 : 2
S04_H2O	16.1	1 : 5
SO4_PO4	11.1	1 : 9
S04_0	11.1	1 : 15
S04_2	3.7	1 : 45
S04_4	11.1	1 : 12
S04_8	3.7	1 : 137
S04_16	4.9	1 : 177
S04_32	9.9	1 : 2
C_TOT	11.1	1 : 4
N_TOT	0.0	—
S_TOT	38.3	1 : 7

[a] Percentage of samples outside window boundaries.

[b] Ratio of outside-window to overall bias.

only one laboratory analyzed these samples and no accuracy windows were available. Also, elemental analysis of C_TOT, N_TOT, and S_TOT did not exhibit interlaboratory differences because the analyses were performed only at Laboratory 2.

For the physical parameters, VFS and CLAY had the highest laboratory differences from the reference values. For pH, all laboratory differences were two percent or less, and represented the lowest differences overall for any parameter group. For the cations in ammonium chloride, MG_CL and K_CL had the highest and lowest differences, respectively. For the cations in ammonium acetate, NA_OAC and CA_OAC had the highest and lowest differences, respectively. For the CEC parameters, differences for CEC_OAC were somewhat higher than for CEC_CL. For the cations in calcium chloride, FE_CL2 and CA_CL2 had the highest and lowest differences, respectively. For extractable iron and aluminum, FE_PYP and AL_PYP had the highest differences. The differences were less than ten percent for the extractable sulfate parameters and less than five percent for the sulfate isotherm parameters.

Generally, Laboratory 1 showed the smallest differences and Laboratory 4 showed the largest differences. Across all parameters, the laboratories showed the lowest differences for the pH parameters and the highest differences for CLAY and FE_CL2.

As a summary assessment for laboratory differences, an average laboratory difference from the pooled reference value was calculated for each parameter group. The laboratory differences were all less than six percent of their respective pooled reference values except for the data from Laboratory 1 for the cations in ammonium acetate and the data from Laboratory 4 for the cations in calcium chloride; both average differences were approximately 10 percent.

Table 3-13 also shows the laboratories that had significant differences identified by Scheffe's pairwise multiple comparison test of laboratory means. Results from the paired comparisons are presented for laboratories which were significantly lower, defined at the .05 level of significance, than one or both of the other laboratories. About 54 percent of the parameters (25 of 46 parameters) showed significant laboratory differences. Four of the parameters (SILT, PH_002M, CEC_OAC, and SI_AO) showed all three laboratories to be significantly different from each other. There were three parameters where Laboratory 1 was significantly different from the other two laboratories, five parameters for Laboratory 4 and six parameters for Laboratory 2.

There was no consistent pattern of differences for any specific laboratory in most of the parameter groups. However, for the cations in calcium chloride, Laboratory 2 was significantly different from the other laboratories in all cases shown. For the sulfate isotherm parameters, Laboratory 4 was significantly lower than the other laboratories in all four of the cases that showed differences. These latter two results indicate that, despite all laboratories adhering to specified protocols in a strictly controlled QA program, a laboratory can show a consistent significant difference from other laboratories in its submitted data and still satisfy the batch acceptance criteria.

Table 3-13 also presents the average deviation from the reference value, expressed in the parameter reporting units, for each parameter and laboratory. These values indicate the expectation of the absolute deviation, without regard to sign, exhibited by each laboratory as a function of bias and imprecision in relation to the reference value for each parameter. Only five parameters were significantly large, i.e., the ratio of the squared deviation to the variance of the prior reference distribution was greater than 3:1. These parameters included AL_PYP and SO4_PO4 for Laboratory 1, COSI and FSI for Laboratory 2, and PH_002M for Laboratory 4.

Laboratory Trends

Plots of the laboratory moving averages for the laboratory audit samples are presented in Appendix I. The plots occasionally depict situations when a particular laboratory showed an upward, downward, or irregular trend over time for a given parameter. The Y-axes of the plots are expressed in divisions of reporting units but are not enumerated because the

Table 3-13. Analytical Laboratory Differences Pooled Across the Laboratory Audit Samples

Parameter	Reporting units	Percent difference from R			Pairwise lab difference[a]	Average deviation from R			R value
		L1	L2	L4		L1	L2	L4	
		percent				units			– units –
SAND	wt %	-1	5	-3	4 < 1,2	1.41	3.37	3.52	55.65
VCOS	"	11	11	8		1.17	1.05	2.02	3.95
COS	"	12	4	11		1.82	1.31	3.43	8.61
MS	"	3	4	5		1.00	1.53	1.78	14.26
FS	"	-7	3	-6	4 < 2	2.10	1.20	3.18	16.51
VFS	"	-7	6	-19		1.49	2.54	2.83	12.30
SILT	"	4	-5	9	2 < 1 < 4	2.81	3.81	5.39	39.81
COSI	"	6	-10	8	2 < 1,4	2.47	5.71*	3.31	20.94
FSI	"	-1	-2	7		1.08	5.27*	2.55	19.27
CLAY	"	-18	6	-36	4,1 < 2	0.95	1.97	1.95	3.91
PH_H20	pH units	-1	1	-2	4 < 1 < 2	0.11	0.07	0.15	5.14
PH_002M	"	1	2	-1	4 < 1	0.13	0.13	0.21*	4.71
PH_01M	"	-1	-1	-1		0.07	0.05	0.07	4.56
CA_CL	meq/100g	3	-3	-3	4,2 < 1	0.04	0.02	0.02	0.23
MG_CL	"	12	-10	4	2 < 4,1	0.02	0.01	0.01	0.05
K_CL	"	-1	5	1		0.01	0.01	0.00	0.06
NA_CL	"	-7	-5	-1		0.01	0.01	0.00	0.03
AL_CL[b]	"	-3	2	-1		0.54	0.17	0.18	3.53
CA_OAC	meq/100g	6	-2	-3	4,2 < 1	0.03	0.03	0.02	0.20
MG_OAC	"	7	-2	-2		0.01	0.02	0.01	0.05
K_OAC	"	12	11	11		0.01	0.01	0.01	0.05
NA_OAC	"	16	12	17	2 < 1	0.01	0.01	0.01	0.03
CEC_CL	meq/100g	-1	-1	-1		0.19	0.36	0.52	4.11
CEC_OAC	"	3	-13	-1	2 < 4 < 1	1.54	1.96	1.80	11.83
AC_BACL	"	-6	-4	8	2,1 < 4	1.68	1.84	2.30	15.40
CA_CL2	meq/100g	5	1	6	2 < 1	0.07	0.06	0.05	0.61
MG_CL2	"	1	7	12		0.01	0.01	0.01	0.04
K_CL2	"	-9	15	3	1,4 < 2	0.00	0.00	0.00	0.01
NA_CL2	"	2	6	8		0.01	0.00	0.00	0.02
FE_CL2	"	-11	-36	2	2 < 4,1	0.00	0.00	0.00	0.01
AL_CL2	"	16	-10	27	2 < 4,1	0.01	0.01	0.01	0.02
FE_PYP	wt %	-1	-2	-8	4 < 1,2	0.04	0.04	0.06	0.50
AL_PYP	"	4	-2	-5	2,4 < 1	0.07*	0.03	0.05	0.48
FE_AO	"	1	2	1		0.08	0.09	0.06	0.67
AL_AO	"	1	-1	1	2 < 1	0.06	0.04	0.07	0.78
SI_AO[b]	"	-7	7	-1	1 < 4 < 2	0.04	0.05	0.01	0.32
FE_CD	"	-1	3	1		0.13	0.09	0.04	1.10
AL_CD	"	-4	4	2		0.07	0.08	0.06	0.59
SO4_H2O	mg S/kg	2	1	1		2.11	1.10	1.91	12.11
SO4_PO4	"	7	4	-1		12.96*	7.57	4.69	62.17
SO4_0	mg S/L	4	3	1		0.13	0.11	0.11	1.26
SO4_2	"	4	1	1		0.14	0.12	0.13	2.53
SO4_4	"	3	3	-2	4 < 1,2	0.19	0.19	0.18	3.87
SO4_8	"	3	1	-1	4 < 1	0.27	0.18	0.40	6.61
SO4_16	"	4	1	-3	4 < 2 < 1	0.73	0.40	0.69	12.84
SO4_32	"	2	3	-4	4 < 1,2	1.12	1.35	1.84	26.07

[a] Significant at the .05 level of significance by Scheffe's multiple comparisons test.

[b] Based on differences for B horizon FAP samples only.

* Significantly high (> 3:1) ratio of squared deviation to variance of the prior reference value (R) distribution.

window boundaries have been kept confidential to ensure future use of the soil audit samples in other programs.

Generally, the trend data for the audit samples were well within the accuracy windows for most parameters and, in most cases, approached the reference values. There were a few exceptions, e.g., MG_CL2 for the C horizon audit sample and K_OAC for the Bw horizon audit sample, where the laboratories were grouped near the upper boundary of the accuracy window. This indicates that the window boundaries used for the MASS might not have entirely represented the audit sample concentrations or that the changes in analytical procedures for the MASS possibly affected the comparability of analytical results between the MASS and the previous DDRP surveys from which the windows were calculated.

There were also parameters, e.g., AC_BACL for the B horizon audit sample, where one laboratory showed a tendency for its data to be substantially farther from the central tendency of the window than the other laboratories, possibly indicating that the laboratory was experiencing difficulty with the analysis. In many cases, e.g., SILT for the B horizon audit sample, a general converging central tendency was observed over time. This could indicate that the laboratories were gaining analytical experience at the possible expense of the survey or that the QC program was effectively keeping the laboratories in control of the analysis. There were also a few parameters, e.g., CEC_OAC for the B horizon audit sample and CA_OAC for the Bw horizon audit sample, where a laboratory would initially exceed the window boundaries and subsequently reverse the trend to fall within the window. This pattern suggests that the QA program was successful in controlling between-batch measurement quality.

Finally, there were several parameters, e.g., SO4_8 and FE_CL2 for the C horizon audit sample, where the data converged near the reference value although the boundaries of the window were relatively wide. This pattern was most evident for the parameters which were analyzed by a single laboratory, e.g., N_TOT for the Bw horizon audit sample.

The trend plot for S_TOT shows an extremely wide scatter of data outside of the accuracy window for the Bw horizon audit sample (see Figure I-50 in Appendix I). This characteristic did not initially cause concern because there was no particular trend associated with the scatter, and the overall QART acceptance criteria were satisfied. The subsequent assessment of bias, however, indicated an inordinately high percentage of observations outside of the window, as shown previously in Table 3-12. The QA staff discovered that the Bw horizon window boundaries for this parameter had been calculated incorrectly and were very narrow in relation to the normal scatter of the data and in relation to the other laboratory audit samples. If real-time assessment of control charts had been a priority procedure, such an irregular outside-window scatter would have been evaluated and monitored. Fortunately, the uniform application of the QART criteria enabled the QA staff to ensure control of the laboratories' sulfur analysis and the resulting S_TOT data had acceptable accuracy. Recalculation of the Bw horizon accuracy window indicated that all of the S_TOT data would have been within the boundaries of the corrected window. This is a good example of the usefulness of control charts for real-time assessment and for guiding the adjustment of the QA program and acceptance criteria as a survey progresses.

Assessment of Representativeness

All pedons sampled were within the range of morphological characteristics outlined in their respective sampling classes (Kern and Lee, in press). Hence, the MQO for representativeness of the field sampling was satisfied.

The homogenization and subsampling procedures at the preparation laboratory produced representative analytical soil samples of known and accepted quality (Papp and Van Remortel, in press). More information on this characteristic of the data can be found in the precision discussions of this report, where assessments of the preparation duplicates are made.

Histograms of the range and frequency distribution of the routine samples, field duplicates, preparation duplicates, and natural audit samples for each of the parameters are presented in Appendix G. The analyte concentrations in the field duplicates generally were representative of the routine sample concentrations. This was important in defining the confidence a user will have of the data uncertainty estimates calculated from these two data sets. The exceptions were mainly observed in the cations and the extractable sulfate parameters, and are presented in Table 3-14. A set of P_{05}, P_{50}, and P_{95} percentiles are provided in the table as benchmark values for the distributions. Of the 15 parameters identified, most are representative of the range of concentration but not of the distribution within the range. The analyte concentrations in the preparation duplicates generally were representative of the field duplicate concentrations because the preparation duplicates were subsampled directly from the field duplicates. The audit samples usually encompassed the overall range of data from the routine samples.

Assessment of Completeness

Soil sampling protocols specified the sampling of all designated pedons. All of the 150 pedons initially selected were sampled, resulting in 100 percent completeness (Kern and Lee, in press). As specified in the preparation laboratory protocols, each batch of samples sent to an analytical laboratory contained the appropriate measurement quality samples, including a pair of preparation duplicate samples that were split from a field duplicate and its respective routine sample. The required soil analyses and sample processing tasks at the preparation laboratory were performed on 100 percent of the field bulk soil samples that satisfied the sample receipt verification criteria (Papp and Van Remortel, in press).

The number of AO flags and J, M, or X tags assigned to the 844 routine samples was used to assess analytical completeness of the MASS verified data base. These flags and tags denoted missing data and lack of sufficient sample for analysis, respectively (Papp et al., 1989). There were no such flags or tags assigned to the verified data base, indicating completeness of 100 percent for analysis of all parameters as shown in Table 3-15. This satisfied the MQO of 90 percent for analytical completeness.

Five levels of confidence, ranging from 0 to 4, were assigned during data validation activities to segregate and classify data in the validated data base. Data exhibiting levels of confidence of 0, 1, or 2, i.e., data appended with fewer than two major flags or fewer than one major and two minor flags, were used to assess completeness in the validated data base (Turner et al., in preparation). Completeness of 98.6 percent or higher for all parameters was achieved for the validated data, as documented in Table 3-15.

Assessment of Comparability

The comparability issues of primary importance to the quality of the DDRP data bases are the: (1) statistical methods, (2) types of measurement quality samples used to evaluate the quality attributes, (3) sampling, preparation, and analytical methods, and (4) the user-defined data acceptability criteria. If these characteristics are comparable among the three DDRP surveys, a quantitative comparison of differences among the surveys allows the user to discern which data may not be comparable for a given purpose.

Comparison of Statistical Methods

During the data analysis phase of the NE and SBRP surveys, it was observed that the error variance for most parameters was a function of analyte concentration (Van Remortel et al., 1988; Byers et al., 1989). The initial statistical analysis of the NE region data was performed using a logarithmic transformation of the analytical data for each parameter. This approach tended to inflate the error estimate for low concentration samples in an inordinate manner. In the SBRP and MASS analysis, a step function was used to estimate error variance such that each step value represented an error variance for a specific concentration interval. The NE data were subsequently re-evaluated using this approach so that the statistical analysis would be consistent among all three surveys.

Comparison of Measurement Quality Samples

Five audit samples (Oa, A, Bs, Bw, and C horizons) were used for QE purposes in the NE and SBRP surveys, and four audit samples (O, B, Bw, and C horizons) were used in the MASS. It was discovered at the end of the

Table 3-14. Significant Differences in the Distribution of Field Duplicates in Relation to the Routine Samples

Parameter	Data Set[a]	n	Mean	P_{05}[b]	P_{50}[b]	P_{95}[b]	KS-Stat[c]
MG_CL	RS	844	0.48	0.01	0.13	1.99	-
	FD	58	0.30	0.01	0.04	1.84	0.279
K_CL	RS	844	0.17	0.03	0.10	0.50	-
	FD	58	0.10	0.03	0.07	0.30	0.264
NA_CL	RS	844	0.02	0.00	0.01	0.06	-
	FD	58	0.02	0.00	0.01	0.11	0.190
MG_OAC	RS	844	0.46	0.01	0.13	1.94	-
	FD	58	0.27	0.01	0.05	1.63	0.280
K_OAC	RS	844	0.17	0.03	0.10	0.50	-
	FD	58	0.10	0.03	0.07	0.29	0.263
NA_OAC	RS	844	0.02	0.00	0.01	0.06	-
	FD	58	0.02	0.00	0.01	0.13	0.193
CEC_CL	RS	844	8.28	2.73	7.05	19.79	-
	FD	58	7.63	2.42	5.21	24.41	0.230
CA_CL2	RS	844	0.65	0.33	0.54	2.07	-
	FD	58	0.73	0.46	0.57	2.69	0.263
MG_CL2	RS	844	0.12	0.01	0.06	0.41	-
	FD	58	0.09	0.01	0.03	0.57	0.266
K_CL2	RS	844	0.05	0.01	0.02	0.16	-
	FD	58	0.03	0.00	0.02	0.18	0.201
FE_CL2	RS	844	0.01	0.00	0.00	0.04	-
	FD	58	0.01	0.00	0.00	0.04	0.467
AL_CL2	RS	844	0.11	0.00	0.09	0.27	-
	FD	58	0.11	0.00	0.11	0.23	0.189
FE_PYP	RS	844	0.35	0.04	0.24	1.05	-
	FD	58	0.33	0.11	0.26	0.99	0.208
SO4_H2O	RS	844	18.33	2.22	12.18	31.71	-
	FD	58	19.28	4.93	14.21	43.60	0.222
SO4_PO4	RS	844	50.28	5.06	30.23	136.92	-
	FD	58	53.07	16.73	45.65	139.02	0.278

[a] RS = routine samples; FD = field duplicates.

[b] P_{05}, P_{50}, and P_{95} are the 5th, 50th, and 95th percentiles by data set.

[c] Kolmogorov-Smirnov statistic, significant at the .05 level; critical value for FD/RS = 0.185.

SBRP survey that there were insufficient quantities of Oa, A, and Bs audit samples remaining for use as QE samples in the MASS, so a recently collected B horizon audit sample was substituted. The Oa and A horizon audit samples were used for QC purposes in the MASS, while the Bs horizon audit samples were used as QE samples at the preparation laboratory (Papp and Van Remortel, in press).

In the MASS, field audit samples were included in each sample batch. Mineral soil batches contained a FAL sample and two FAP samples, and organic soil batches contained three FAO samples. The FAP and FAO samples were used to determine within-batch system precision and accuracy. A single LAL sample was included in each mineral soil batch and was used with the FAL sample to assess contamination and low-range inaccuracy, and to estimate the system detection limits. The use of QCAS samples in the MASS helped to control error at the laboratories. The additional audit samples did not directly affect the comparability of the data from the three surveys, but aided in the QE and QC activities.

The within-batch precision estimate was refined by increasing the number of preparation duplicates from one per batch in the NE to two per batch in the SBRP and MASS. For the MASS, one preparation duplicate was split from the field duplicate and the other from its associated routine sample.

Comparison of Sampling, Preparation, and Analytical Methods

Field sampling for the MASS included the use of standard National Cooperative Soil Survey (NCSS) characterization and sampling procedures, specified protocols, and standard

Table 3-15. Completeness of Routine Data from the Verified and Validated Data Bases

Parameter	Verified data base[a] n	Verified data base[a] percent	Validated data base[a] n	Validated data base[a] percent
MOIST	844	100.0	844	100.0
SAND	795	100.0	791	99.5
VCOS	795	100.0	795	100.0
COS	795	100.0	795	100.0
MS	795	100.0	793	99.8
FS	795	100.0	794	99.9
VFS	795	100.0	794	99.9
SILT	795	100.0	795	100.0
COSI	795	100.0	794	99.9
FSI	795	100.0	793	99.8
CLAY	795	100.0	789	99.3
PH_H20	844	100.0	844	100.0
PH_002M	844	100.0	843	99.9
PH_01M	844	100.0	842	99.8
CA_CL	844	100.0	837	99.2
MG_CL	844	100.0	839	99.4
K_CL	844	100.0	833	98.7
NA_CL	844	100.0	836	99.0
AL_CL	844	100.0	837	99.2
CA_OAC	844	100.0	844	100.0
MG_OAC	844	100.0	843	99.9
K_OAC	844	100.0	839	99.4
NA_OAC	844	100.0	839	99.4
CEC_CL	844	100.0	840	99.5
CEC_OAC	844	100.0	840	99.5
AC_BACL	844	100.0	842	99.8
CA_CL2	844	100.0	839	99.4
MG_CL2	844	100.0	844	100.0
K_CL2	844	100.0	839	99.4
NA_CL2	844	100.0	837	99.2
FE_CL2	844	100.0	832	98.6
AL_CL2	844	100.0	841	99.6
FE_PYP	844	100.0	844	100.0
AL_PYP	844	100.0	844	100.0
FE_AO	844	100.0	844	100.0
AL_AO	844	100.0	844	100.0
SI_AO	844	100.0	844	100.0
FE_CD	844	100.0	844	100.0
AL_CD	844	100.0	844	100.0
SO4_H2O	844	100.0	839	99.4
SO4_PO4	844	100.0	835	98.9
SO4_0	795	100.0	793	99.8
SO4_2	795	100.0	794	99.9
SO4_4	795	100.0	792	99.6
SO4_8	795	100.0	794	99.9
SO4_16	795	100.0	794	99.9
SO4_32	795	100.0	794	99.9
C_TOT	844	100.0	842	99.8
N_TOT	844	100.0	843	99.9
S_TOT	844	100.0	844	100.0

[a] The total routine samples (N) is 844; for particle size and sulfate isotherm analyses, N is 795. For verified data base, n is samples that underwent analysis; for validated data base, n is cumulative samples valid at level of confidence 0, 1, or 2.

reporting forms which ensured that the resulting data would be comparable with data generated from the NE and SBRP sampling activities. Because of an unclear protocol in the NE survey, some sampling crews collected a field duplicate using the alternate trowel-full method that was intended, while other crews collected a field duplicate by splitting a composite bulk soil sample. The protocol was clarified for the other two surveys. As a result, the field sampling within-batch variability is expected to be smaller in the NE survey than in the SBRP or MASS surveys because much of the sampling error is masked in the NE field duplicates (Van Remortel et al., 1988). Since the routine samples for all three surveys were collected using similar protocols, the resulting field data can be compared.

Nearly identical soil preparation methods were used throughout the three surveys, although the NE protocols were revised for clarity in the SBRP survey and again in the MASS (Appendix A in Haren and Van Remortel, 1987; Appendix A in Papp and Van Remortel, in press). There were a few differences in the preparation methods, e.g., the number of passes through a riffle splitter during homogenization was seven in the NE and SBRP surveys and five in the MASS. There were also differences inherent in the use of more than one preparation laboratory, e.g., different types of sample drying facilities with varying airflow and humidity conditions. The preparation laboratory operations were consolidated from four laboratories in the NE survey and two laboratories in the SBRP survey to a single MASS laboratory.

In the MASS, seven physical and chemical analyses were performed at the preparation laboratory: field-moist pH, air-dry moisture content, organic matter by loss-on-ignition, percent fine gravel, percent medium gravel, and bulk density determined by clod and known volume methods. The field-moist pH, organic matter, and known volume bulk density parameters were not measured in the NE and SBRP surveys.

Five of the 53 analytical parameters measured over the course of the DDRP were measured in only one or two of the three surveys, therefore, the data from these five parameters are not directly comparable across all surveys. In each case, however, the data generally satisfied the acceptance criteria for precision, as there were no accuracy criteria defined for these parameters. These parameters are the specific surface area (SP_SUR) and the exchangeable acidity and aluminum in potassium chloride (AC_KCL and AL_KCL) parameters measured only in the NE and SBRP surveys, and the extractable silicon in acid oxalate (SI_AO) and exchangeable aluminum in ammonium chloride (AL_CL) parameters measured only in the MASS.

There was one complete method change and several modifications made in the DDRP analytical methods prior to the MASS sample analysis. One of the extractants for aluminum was changed from 1M potassium chloride (AL_KCL parameter) to 1M ammonium chloride (AL_CL parameter). When extracting calcium with calcium chloride, samples were shaken overnight instead of being extracted on a mechanical extractor (all _CL2 parameters). The procedure for exchangeable cations and cation exchange capacity included a two-fold increase in the amount of soil relative to the solution volume (all _CL and _OAC parameters). The volume specificity in the exchangeable acidity procedure was more precise (AC_BACL parameter). The initial concentration range requirements for the sulfur solution standards used in the isotherm measurements were more stringent (SO4_0 - 32 parameters). Instrumentation requirements were more specific for the majority of the analyses.

Comparison of User-Defined Acceptability Criteria

Assessing the comparability of data collected during the three DDRP surveys was complicated by differences in the protocols and MQOs across the surveys. User-defined data acceptability is reflected in the precision and accuracy objectives and the overall utility of data that have satisfied the defined objectives. The precision and accuracy objectives and acceptance criteria were modified, i.e., usually tightened, for the MASS because of experience gained during the NE and SBRP surveys. The use of accuracy windows in the MASS also improved the data evaluation procedures.

There were several differences in the MQOs between the NE and SBRP surveys and the MASS, and overall measurement quality generally is better in the MASS data bases. Therefore, it is possible that some of the NE and SBRP data may not be suitable for the same data analysis procedures performed on the MASS data without some form of caveat. Possible examples include the specific surface data and the organic soil sulfate isotherm data from the NE and SBRP surveys which are not being utilized by some data users.

Quantitative Comparison of the DDRP Surveys

Data from the Bw audit sample were used for general quantitative survey comparisons because the Bw was the only median-range audit sample used for QE purposes in all three surveys. For each parameter, pooled mean values for the Bw horizon audit samples were initially compared across surveys using an F test as part of ANOVA. Because a large number of parameters showed a significant difference among surveys at the .05 level, the differences were compared to the existing accuracy windows to determine whether any of the survey mean values exceeded the limits of the windows. It was determined that most of the mean values were safely within the accuracy windows. As a way to alert data users to possible comparability constraints, the QA staff used Scheffe's multiple comparison test to identify specific differences in the survey mean values highlighted at the .01 level of significance, as presented in Table 3-16. Only 10 parameters showed differences among surveys at this level: AL_CL vs. AL_KCL, SO4_H2O, SO4_0, SO4_2, SO4_4, CA_CL2, COSI, FE_CD, and C_TOT. Although 40 of the 50 parameters (80 percent) common to all three surveys were not significantly different at this level of significance across surveys, data users should exercise caution when using data from these 10 parameters.

An important difference observed was between the AL_CL and AL_KCL parameters. The NE and SBRP mean values for AL_KCL were approximately the same but the MASS mean value for AL_CL was highly significantly different. This finding possibly reflects the change in extractant for exchangeable aluminum from 1M potassium chloride used in the NE and SBRP surveys to 1M ammonium chloride used in the MASS. The sulfate parameter differences were largely attributed to the greater uncertainty in the standard solution

Table 3-16. Multiple Comparison of Interlaboratory Mean Values Using the Bw Audit Sample

Parameter	Reporting units	Interlaboratory mean for Bw sample NE	SBRP	MASS
MOIST	wt %	2.12	2.33	2.34
SAND	"	28.10	27.06	25.40
VCOS	"	3.02	2.62	2.49
COS	"	4.07	4.04	3.77
MS	"	3.62	3.51	3.55
FS	"	4.13	3.91	4.23
VFS	"	13.26	13.01	11.40
SILT	"	64.86	65.45	68.65
COSI**	"	31.09^{A}	$33.71^{A,B}$	36.32^{B}
FSI	"	33.75	31.73	32.34
CLAY	"	7.05	7.48	5.95
PH_H2O	pH units	5.08	5.13	5.07
PH_002M	"	4.71	4.72	4.74
PH_01M	"	4.54	4.62	4.57
CA_CL	meq/100g	0.27	0.29	0.27
MG_CL	"	0.05	0.05	0.06
K_CL	"	0.06	0.06	0.06
NA_CL	"	0.04	0.02	0.03
AL_CL-KCL**	"	1.53^{A}	1.42^{A}	1.84^{B}
CA_OAC	meq/100g	0.25	0.24	0.25
MG_OAC	"	0.05	0.06	0.06
K_OAC	"	0.06	0.06	0.06
NA_OAC	"	0.03	0.02	0.03
CEC_CL	meq/100g	5.18	5.79	4.38
CEC_OAC	"	12.54	13.12	10.99
AC_BACL	"	17.33	17.22	16.39
CA_CL2**	meq/100g	0.51^{A}	$0.60^{A,B}$	0.62^{B}
MG_CL2	"	0.03	0.04	0.04
K_CL2	"	0.01	0.01	0.01
NA_CL2	"	0.02	0.02	0.02
FE_CL2	"	0.001	0.001	0.001
AL_CL2	"	0.004	0.004	0.010
FE_PYP	wt %	0.81	0.85	0.75
AL_PYP	"	0.57	0.58	0.54
FE_AO	"	1.03	1.03	0.99
AL_AO	"	0.91	0.88	0.86
FE_CD**	"	1.56^{A}	1.88^{B}	$1.72^{A,B}$
AL_CD	"	0.62	0.67	0.63
SO4_H20**	mg S/kg	20.46^{A}	22.89^{B}	20.31^{A}
SO4_PO4	"	105.77	108.97	109.44
SO4_0**	mg S/L	2.00^{A}	2.27^{B}	2.05^{A}
SO4_2**	"	2.93^{A}	3.22^{B}	$3.04^{A,B}$
SO4_4**	"	3.86^{A}	4.30^{B}	$4.09^{A,B}$
SO4_8	"	6.18	6.54	6.34
SO4_16	"	11.32	11.91	11.87
SO4_32	"	23.78	23.70	24.13
C_TOT**	wt %	1.56^{A}	$1.51^{A,B}$	1.45^{B}
N_TOT	"	0.121	0.110	0.113
S_TOT	"	0.019	0.019	0.020

^{A} ^{B} Pairwise differences among surveys highlighted for significant differences at the .01 level.

** Significant at the .01 level based on Scheffe's multiple comparison test.

concentrations for the NE and SBRP surveys. The modified protocol in the MASS resulted in more accurate initial sulfur extraction solutions. The procedural change from mechanical extractor to overnight shaking for the determination of CA_CL2 in the MASS did not appear to have a significant effect, as the mean values from the SBRP and MASS were not very different.

Differences in the data due to treatment effects of different preparation and analytical laboratories were present in all comparisons of the data. For example, it was noted in the MASS that the fine silt fraction was not completely separated from the coarse silt fraction during the early stages of analysis at Laboratory 2. This could be a contributing factor to the higher COSI mean in the MASS. The significant differences across surveys observed for FE_CD and C_TOT cannot be completely explained on the basis of differences among laboratories. Differences in the instrumentation used to measure C_TOT in the surveys may also have had an effect.

Interlaboratory Comparison Study

The objective of the interlaboratory comparability study was to determine whether the analytical data for soil audit samples analyzed by contract soil characterization laboratories for the DDRP soil surveys are comparable to data for the same samples analyzed by other soil characterization laboratories in the United States and Canada.

The original four DDRP laboratories constituted the "DDRP" laboratory group that used analytical methods and procedures as specified in the NE and SBRP contractual statements of work. Data from these laboratories were collected in 1985 and 1986. Two of the original four laboratories were selected to represent the DDRP laboratories in the study. Fifteen randomly selected soil characterization laboratories, including nine in the United States and six in Canada, were selected to represent the non-contract or "external" laboratory group. These two DDRP laboratories followed the actual methods and procedures used in the NE and SBRP surveys, while each of the external laboratories used similar methods but followed its own specific procedure. In 1988, each laboratory analyzed two batches containing six audit samples per batch, with a two-month interval between batches. The audit samples included six different soil horizon types (A, B, Bs, Bw, C, and O) from the eastern United States which had been previously analyzed for all 51 analytical parameters in the NE and SBRP surveys. Each laboratory analyzed two blind replicates of each sample.

Audit sample data for each parameter were analyzed for various attributes using primarily youden-pair plots (Youden, 1985) appropriate *F* and *t* statistics. These tests examined the comparability between the DDRP and external laboratory groups. The attributes investigated were time effect, homogeneity of data between the two groups, protocol variability, and between-group variability. Summary statistics were also derived for each soil parameter by combining data across audit sample horizons and for each parameter group by combining appropriate parameters.

The temporal effects of possible degradation, contamination, or procedural changes on the audit samples were assessed by comparing the DDRP data collected in 1985-86 with the external data collected in 1988. The two participating DDRP laboratories in the external group provided the link needed to make this assessment. There was no time effect observed in the data generated from this comparison. Hence, there is no evidence that the soil chemical and physical characteristics changed due to degradation, contamination, or changes in laboratory analytical techniques. This implies that there was no soil contamination or degradation under the 4°C storage conditions and that, if the soils for other prospective data bases were prepared and stored prior to analysis in a similar manner as the DDRP protocols, then the two sets of data can be compared.

The homogeneity of laboratory data and protocol variability between DDRP and the external laboratories were greater for certain cations and certain soil types. For example, the DDRP appeared to achieve greater accuracy at the lower concentrations for such cations as potassium and sodium for all soil types tested. The differences were revealed not because the other laboratories did not exhibit good results, but because the DDRP laboratories as a group were very accurate and precise due to exceptionally tight QE and QC criteria and consistent analytical procedures among laboratories. The difference merely reveals that the analytical procedures used by the external laboratories are somewhat variable, though not significantly so in most cases. A large percentage of laboratories used analytical procedures that were very similar to the DDRP procedures for most parameters.

The analytical data for the DDRP laboratories were within the ranges generated by the independent external laboratories and, therefore, are generally comparable among the two groups. The results for most parameters indicate that the somewhat diverse analytical procedures are quite robust within a given analytical method. The parameters were also classified into ten parameter groups and the analytical results at this level are comparable between the DDRP and external data with no exceptions. The detailed results of the interlaboratory comparison study are contained in a separate report (Fenstermaker et al., in preparation).

Assessment of Data Uncertainty Components

The following subsections describe various data uncertainty components that are estimated using data from the measurement quality samples. The magnitude of measurement uncertainty in relation to overall data uncertainty is also assessed.

Additive Components of Uncertainty

As described previously in Section 2, the within-batch precision estimates were pooled over the concentration range using the proportion of routine data in each interval to derive the within-batch precision component of the δ values (see Appendix C). It was assumed that each laboratory analyzed the soil samples on a batch-by-batch basis under conditions specific to each batch analysis; hence, the between-batch variability was calculated for each parameter using the data from the LAP samples. The bias was demonstrated to be quantifiable using the LAL samples and the means of the LAP sample pairs, although it was small for most parameters. The within- and between-batch variances were added to the squared bias term and were converted into reporting units to produce delta values for each data set and parameter. Table 3-17 shows the bias and imprecision estimates and the contribution of the between-batch and bias components in relation to the within-batch imprecision estimates for each parameter for the analytical component. Ratios are used to indicate the parameters which show a considerable contribution of the between-batch or bias components in relation to the within-batch component.

The within- and between-batch mean sums of squares and the squared bias component of analytical uncertainty can be experimentally compared with the three mean squares of a randomized block design. In this scenario, both the expected value of the squared bias and expected value of the between-batch mean square include the expected value of the within-batch mean square (Box et al., 1978). If the between-batch mean square is two times larger than the within-batch mean square, then the actual between-batch imprecision can be inferred to be as large as the within-batch imprecision. Similarly, if the between-batch mean square is more than three times larger than the within-batch mean square, then the between-batch imprecision can be inferred to be significantly larger than the within-batch imprecision. Hence, if the ratio of the between-batch component with the within-batch component in reporting units exceeds $\sqrt{3}$, i.e., 1.73, then the between-batch imprecision can be considered significant in relation to the within-batch imprecision. The same criteria can be used to examine the significance of the bias in relation to the within-batch imprecision.

Under this framework, there is no evidence of significant between-batch or bias uncertainty in relation to within-batch uncertainty if the ratio is less than 1. If the ratio is between 1 and 1.73, the observed uncertainty is negligible and could be due to random fluctuation. If the ratio is greater than 1.73, then the between-batch or bias component could be as large as 50 percent of the within-batch component.

The ratio of between-batch to within-batch was greater than 1.73 for four particle size parameters (SAND, COS, FS, and VFS), all three pH parameters (PH_H2O, PH_002M, and PH_01M), two cations from the calcium chloride parameter group (CA_CL2 and K_CL2), and three sulfate isotherm parameters (SO4_2, SO4_8, and SO4_16). Possible reasons for these parameters to show substantial between-batch error could relate to: (1) the unique aspects of their methods of analysis, e.g., the particle size parameters, or variability in the spiking solutions or equilibrium conditions, e.g., temperature, for the sulfate isotherm parameters; (2) very low soil concentrations, e.g., the cations in calcium chloride; (3) a very precise within-batch imprecision estimate which magnified the effect of between-batch imprecision and resulted in a high ratio; or (4) a wide range of acceptable values in the accuracy windows. For the pH parameters, for example, the within-batch component was so small that the between-batch component was substantial. In actuality, both types of uncertainty are low when compared to the within-batch MQO. Therefore, although the contribution of the between-batch uncertainty to total analytical uncertainty might be substantial, the magnitude of the uncertainty is relatively small. This conclusion also applies to the CA_CL2 and K_CL2 parameters.

The bias was a relatively minor component of uncertainty, and all ratios of bias to within-batch imprecision were below the critical value of 1.73. In many cases, bias was only a small fraction of the within-batch imprecision.

Effect of Measurement System on Data Uncertainty

Table 3-18 provides the δ values of data uncertainty for the analytical parameters. As expected, the estimates increased in a progressive manner from δ_1 through δ_4 which are based on the LAP, PD, FD, and S/H data sets, respectively. The δ_1 values contain analytical laboratory uncertainty confounded with audit sample preparation uncertainty. The δ_2 values contain the confounded uncertainty of sample preparation and analysis. The δ_3 values contain the confounded overall measurement uncertainty of field sampling, preparation, and analysis. The δ_4 values contain uncertainty due to the spatial heterogeneity of the routine sample population confounded with the overall measurement uncertainty of sampling, preparation, and analysis.

It has been proposed that a measured value can be considered as essentially

Table 3-17. Comparison of Measurement Uncertainty Components

Parameter	Reporting units	Within-batch SD ——— units ———	Between-batch SD ——— units ———	Bias - units -	Ratio[a] B-B/W-B	Ratio[b] Bias/W-B
SAND	wt. %	1.160	2.455	0.327	2.1*	0.3
VCOS	"	0.912	0.993	0.402	1.1	0.4
COS	"	0.664	1.528	0.764	2.3*	1.2
MS	"	0.792	1.335	0.567	1.7	0.7
FS	"	0.595	1.779	-0.541	3.0*	0.9
VFS	"	0.665	1.666	-0.810	2.5*	1.2
SILT	"	1.878	2.559	0.890	1.4	0.5
COSI	"	4.055	2.446	0.197	0.6	0.0
FSI	"	4.337	1.808	0.313	0.4	0.1
CLAY	"	1.130	1.153	-0.607	1.0	0.5
PH_H2O	pH units	0.052	0.112	-0.319	2.1*	0.6
PH_002M	"	0.052	0.108	0.028	2.1*	0.5
PH_01M	"	0.032	0.056	-0.021	1.8*	0.7
CA_CL	meq/100g	0.021	0.026	-0.003	1.2	0.1
MG_CL	"	0.012	0.009	0.001	0.8	0.1
K_CL	"	0.004	0.004	0.001	1.1	0.2
NA_CL	"	0.006	0.004	-0.001	0.8	0.2
AL_CL	"	0.411	0.145	-0.062	0.4	0.1
CA_OAC	meq/100g	0.024	0.025	0.000	1.1	0.0
MG_OAC	"	0.014	0.009	0.001	0.6	0.0
K_OAC	"	0.005	0.005	0.006	0.9	1.2
NA_OAC	"	0.005	0.004	0.004	0.8	0.9
CEC_CL	meq/100g	0.306	0.264	-0.123	0.9	0.4
CEC_OAC	"	1.081	1.106	-0.402	1.0	0.4
AC_BACL	"	1.399	1.500	-0.142	1.1	0.1
CA_CL2	meq/100g	0.018	0.038	0.025	2.1*	1.4
MG_CL2	"	0.005	0.006	0.002	1.2	0.5
K_CL2	"	0.001	0.002	0.001	2.0*	0.4
NA_CL2	"	0.005	0.003	0.001	0.7	0.3
FE_CL2	"	0.001	0.001	-0.000	1.1	0.6
AL_CL2	"	0.005	0.006	0.002	1.2	0.5
FE_PYP	wt. %	0.024	0.032	-0.018	1.3	0.7
AL_PYP	"	0.038	0.039	-0.004	1.0	0.1
FE_AO	"	0.041	0.060	0.011	1.4	0.3
AL_AO	"	0.056	0.037	0.002	0.7	0.0
SI_AO	"	0.027	0.031	-0.003	1.1	0.1
FE_CD	"	0.050	0.072	0.012	1.4	0.2
AL_CD	"	0.058	0.055	0.003	0.9	0.1
SO4_H2O	mg S/kg	1.542	0.982	0.126	0.6	0.1
SO4_PO4	"	8.594	6.081	2.009	0.7	0.2
SO4_0	mg S/L	0.085	0.099	0.037	1.2	0.4
SO4_2	"	0.054	0.124	0.045	2.3*	0.8
SO4_4	"	0.107	0.147	0.050	1.4	0.5
SO4_8	"	0.136	0.260	0.052	1.9*	0.4
SO4_16	"	0.295	0.532	0.107	1.8*	0.4
SO4_32	"	0.875	1.078	0.099	1.2	0.1
C_TOT	wt. %	0.209	0.098	-0.034	0.5	0.2
N_TOT	"	0.007	0.004	0.002	0.5	0.2
S_TOT	"	0.002	0.001	-0.001	0.5	0.3

[a] Ratio of between-batch to within-batch variability.

[b] Ratio of bias to within-batch variability.

* Significant between-batch effect.

NOTE: Delta values were not applicable for the MOIST parameter because no windows were available.

Table 3-18. Delta Values and Ratios for Assessment of Uncertainty Components

Parameter	Reporting units	Mean of routine samples	Delta Values[a]				Ratio
			δ_1	δ_2	δ_3	δ_4	$\delta_3 : \delta_4$
SAND	wt %	44.011	3.422^{C}	3.457	4.234	14.557	1 : 3
VCOS	"	4.538	1.330	1.394	1.392	3.824	1 : 3
COS	"	6.172	1.326	1.249	1.439	4.233	1 : 3
MS	"	9.601	1.257^{P}	0.987	1.223	6.112	1 : 5
FS	"	13.930	2.009^{P}	1.959	2.042	8.071	1 : 4
VFS	"	9.762	1.800^{C}	1.806	2.087	5.103	1 : 2
SILT	"	38.157	4.003^{C}	2.881	3.381	10.582	1 : 3
COSI	"	13.183	8.230^{P}	4.812	4.881	7.154	1 : 1
FSI	"	24.969	4.801^{P}	2.635	2.777	8.060	1 : 3
CLAY	"	17.832	2.624^{C}	1.675	1.945	7.553	1 : 4
PH_H2O	pH units	4.703	0.078	0.087	0.114	0.473	1 : 4
PH_002M	"	4.219	0.084^{C}	0.096	0.126	0.440	1 : 3
PH_01M	"	4.013	0.055	0.058	0.079	0.410	1 : 5
CA_CL	meq/100g	1.276	0.030^{C}	0.064^{P}	0.157	1.114	1 : 7
MG_CL	"	0.484	0.015^{C}	0.014	0.031	0.474	1 : 15
K_CL	"	0.171	0.006^{C}	0.008^{P}	0.007^{P}	0.100	1 : 13
NA_CL	"	0.022	0.004^{P}	0.005	0.006	0.012	1 : 2
AL_CL	"	4.542	0.414^{C}	0.310	0.324	2.531	1 : 8
CA_OAC	meq/100g	1.163	0.032^{C}	0.055	0.296	1.091	1 : 4
MG_OAC	"	0.459	0.017^{C}	0.019	0.026	0.446	1 : 17
K_OAC	"	0.172	0.007^{C}	0.011	0.009	0.094	1 : 10
NA_OAC	"	0.020	0.004^{P}	0.005	0.006	0.014	1 : 2
CEC_CL	meq/100g	8.281	0.514^{C}	0.535	0.554	2.858	1 : 5
CEC_OAC	"	13.963	1.407	1.661	1.633	4.667	1 : 3
AC_BACL	"	15.558	1.660^{P}	1.652	1.832	5.582	1 : 3
CA_CL2	meq/100g	0.651	0.042^{C}	0.040	0.040	0.103	1 : 3
MG_CL2	"	0.123	0.007^{C}	0.005	0.008	0.084	1 : 10
K_CL2	"	0.049	0.003^{C}	0.003	0.004^{P}	0.022	1 : 6
NA_CL2	"	0.011	0.004	0.002^{P}	0.002^{P}	0.009	1 : 5
FE_CL2	"	0.014	0.001^{C}	0.002^{P}	0.001^{P}	0.020	1 : 5
AL_CL2	"	0.112	0.009^{C}	0.006	0.009	0.095	1 : 10
FE_PYP	wt %	0.351	0.025^{P}	0.030	0.035	0.305	1 : 9
AL_PYP	"	0.203	0.025^{C}	0.022	0.027	0.165	1 : 6
FE_AO	"	0.348	0.046^{C}	0.033	0.044	0.268	1 : 6
AL_AO	"	0.209	0.022^{P}	0.029	0.036	0.131	1 : 4
SI_AO	"	0.021	0.010^{P}	0.014	0.013	0.029	1 : 2
FE_CD	"	1.836	0.108^{C}	0.289^{P}	0.136^{P}	0.826	1 : 6
AL_CD	"	0.272	0.025^{C}	0.026	0.025	0.125	1 : 5
SO4_H2O	mg S/kg	18.327	1.626^{P}	1.623	1.913	27.173	1 : 14
SO4_PO4	"	50.280	11.877^{C}	6.499	7.665	49.421	1 : 6
SO4_0	mg S/L	2.089	0.105^{P}	0.096	0.137	3.392	1 : 25
SO4_2	"	3.271	0.118^{P}	0.125	0.142	5.325	1 : 38
SO4_4	"	4.504	0.165^{C}	0.154^{P}	0.213^{P}	6.325	1 : 30
SO4_8	"	7.167	0.291^{C}	0.292^{P}	0.377^{P}	5.288	1 : 14
SO4_16	"	13.192	0.604^{C}	0.560	0.624	6.210	1 : 10
SO4_32	"	26.458	1.280^{C}	1.384	1.341^{P}	7.105	1 : 5
C_TOT	wt %	3.212	0.070^{C}	0.060	0.185	1.213	1 : 7
N_TOT	"	0.158	0.003^{C}	0.005	0.008	0.053	1 : 7
S_TOT	"	0.031	0.001^{C}	0.001	0.002^{P}	0.027	1 : 16

[a] δ_1 = calculated from laboratory audit samples; δ_2 = calculated from preparation duplicate samples; δ_3 = calculated from field duplicate samples; δ_4 = calculated from sampling class/horizon groups of routine samples.

^{C} ^{P} Conditional or partial estimate, respectively.

NOTE: Delta values were not applicable for the MOIST parameter because no windows were available.

errorless for most uses if the uncertainty in that value is one-third or less of the permissible tolerance for its use (Taylor, 1987). The QA staff examined the relation of measurement uncertainty to overall data uncertainty in the routine samples in order to provide the data users with a basis for assessing the relative contribution of the measurement system. The δ_3 values calculated from the field duplicate samples (see Appendix C) were compared to the associated δ_4 data uncertainty values generated from the sampling class/horizon groups of routine samples. For the purposes of this assessment, the data uncertainty confounded in the sampling class/horizon groups is considered to be a surrogate for user-defined error tolerance values. Where δ_3 is one-third or less of δ_4, measurement uncertainty is a negligible contribution to the overall data uncertainty.

Under this framework, measurement uncertainty is negligible for 90 percent (44 of the 49 parameters measured) of the data. The five exceptions were the VFS, COSI, NA_CL, NA_OAC, and SI_AO parameters. Two of these parameters are particle size fractions for which no strict precision MQOs were established. As a result of extremely low concentrations, the other three parameters showed high relative measurement uncertainty due to the inordinate effect of measurement error in the low concentration range near the detection limit.

Section 4

Conclusions and Recommendations

Quality Assurance Optimization

A number of improvements were made in the DDRP quality assurance program before and during the Mid-Appalachian Soil Survey in order to provide additional evidence that the various measurement phases of the survey were in statistical control. The quality assurance staff has formulated the following conclusions and recommendations as summary findings from the quality assurance activities for sample analysis conducted in the survey.

Sample Flow

A single preparation laboratory was established in Las Vegas, Nevada, in close proximity to the EPA facility. The one laboratory served as a central control and distribution point for field sampling supplies and resulted in better distribution of samples among sampling crews and laboratories than in previous surveys. It also allowed the establishment and adherence to strictly-defined sample preparation protocols and the ability to track and control progress at the laboratory on a real-time basis. *It is recommended that sample preparation facilities for future surveys continue to be consolidated at a single laboratory to facilitate quality assurance of the samples from the field sampling through the sample analysis phase.*

Mineral and organic samples were placed in separate batches because of differences in analyte concentrations and in the soil to solution ratios required for analysis. The analytical laboratories were able to perform instrument calibrations and sample analyses within narrow linear dynamic ranges. This resulted in improved analytical performance and allowed the quality assurance staff to better control and assess the quality of data generated by the analyses. *It is recommended that mineral and organic samples continue to be placed in separate batches for future surveys.*

Sample Design

A hierarchical sample design was used to gain the maximum information from a manageable number of measurement quality samples. A variety of these samples were used in the field, at the preparation laboratory, and at the analytical laboratories. These samples allowed assessment of preparation laboratory precision and accuracy, analytical and system within- and between-batch precision, and analytical accuracy. *It is recommended that measurement quality samples continue to be distributed among batches and analytical laboratories in such a way as to provide a balanced design for assessment purposes.*

About 25 percent of the soil samples analyzed in the Mid-Appalachian survey were measurement quality samples, at a rate of approximately 10 samples per 40-sample batch. These samples were used to ensure that all phases of the measurement system could be effectively controlled and evaluated. From a logistical and budgetary standpoint, however, this frequency of measurement quality samples would be untenable in many soil analysis projects. A more appropriate level might be 10 to 15 percent.

One obvious way to decrease the percentage of measurement quality samples would be to increase the overall quantity of routine samples in each batch, e.g., from 40 to 60 samples. Advantages of such a move include fewer batches, an immediate reduction in the percentage of measurement quality samples from 25 percent to 17 percent, and a corresponding reduction in the quality assurance costs for data verification. A disadvantage would be a reduction in the available degrees of freedom for statistical estimates of uncertainty across batches.

The quality assurance staff evaluated the utility of the different measurement quality samples used in each mineral soil batch. *It is recommended that the following samples be retained in future surveys because they have demonstrated the greatest benefit in controlling and assessing data quality:*

- one low-range field audit sample for measurement system detectibility, accuracy, and contamination;
- one field duplicate sample for measurement system precision;
- one preparation duplicate sample for preparation precision;
- one low-range laboratory audit sample for analytical detectibility, accuracy, and contamination;
- one pair of median-range laboratory audit samples for analytical precision and accuracy; and
- one median-range liquid audit sample for assessing the soil extraction procedure (not used in batches to date).

Use of this sample design would result in a rate of 7 measurement quality samples per 60-sample batch, i.e., approximately 11 percent. In addition to these seven samples, contractual requirements would specify the analysis of standard in-house quality control samples used by the laboratories to maintain instrument calibration, detectibility, precision, and accuracy for each batch. The data necessary to provide detailed uncertainty estimates would be maintained despite the reduction in the number or percentage of measurement quality samples. The only such samples used in the Mid-Appalachian survey that would be discontinued are the pair of median-range field audit samples and the second of the two preparation duplicates. The quality control audit sample would shift from a "paid" status to a standard internal quality control status.

Data Verification

A computerized data entry and verification system was developed that allowed the calculation of final data values and produced a list of flags and data entry errors for each batch of samples. This system resulted in more rapid turnaround for submission of batch data and completion of the data review and confirmation and reanalysis phases. The computer modem link between the laboratories and the quality assurance staff enabled the rapid transfer of preliminary and final data. *It is recommended that LEVIS or an equivalent data entry and verification system be used in any future soil surveys of this magnitude.*

The verification program evaluated the data with regard to the quality control criteria and other contractual requirements, thereby inducing the laboratories to assume much of the responsibility for identifying and correcting errant data. The use of quality control charts reduced between-batch and between-laboratory uncertainty. Computer evaluation of the double-blind measurement quality samples was accessible only to the quality assurance staff and was used in conjunction with the quality control and summary checks to determine batch acceptance. Sample payment was withheld until all contractual requirements were satisfied, resulting in rapid delivery of data. *It is recommended that these practices be continued.*

Two different internal consistency checks were performed on the routine sample data during the final weeks of data verification for the Mid-Appalachian survey. The first check used pairwise parameter correlations of related parameters to generate a computerized list of possible outlying values called "outliers". The second check utilized the original pedon/horizon configuration of the samples to produce a separate list of possible outliers. An average of three percent of all data values were identified in this manner. The raw data for each outlier were checked by the laboratory managers for transcription errors or other possible errors, e.g., sample switch. Approximately 10 percent of the outliers, i.e., fewer than one-half of one percent of the total data values, were found to be in error. Correction of these data greatly improved the quality of data.

If it can be determined that relationships between pairs of parameters, i.e., linear correlations, are comparable among regions of study, then individual batches of data from new study regions can be incorporated into an overall data file and reviewed in real-time to distinguish outliers for the region. However, if the correlations do not compare among regions, a statistically significant population of data must be collected from the new region before suspect data points from individual batches can be determined to be outliers. The few cases of unacceptable precision nearly always resulted from one or a few inordinate values. Future quality assurance efforts should be directed toward eliminating these outliers. *It is recommended that a method be developed that will clearly identify outlying data points for real-time quality control purposes.*

Data Quality Attributes

Quality assurance experience and changes in analytical methodology allowed the measurement quality objectives for the Mid-Appalachian survey to be, in several cases, more stringent than the objectives for previous DDRP surveys. The resulting data quality for the MASS was generally higher than that of the earlier surveys.

Detectability

The analytical laboratories satisfied the contract requirements for instrument detectability which were based on expected variability in calibration blank samples. After extensive evaluation, it was suggested that the expected variability in low concentration quality control check samples might be a more suitable measure of instrument detectability in future surveys. *It is recommended that the quality assurance staff and data users consider the development of appropriate instrument detectability objectives using the DDRP between-batch data from low concentration quality control check samples instead of calibration blank samples.* Such a move would require more frequent analyses of the check samples in future batches, e.g., one check sample for every 10 routine samples.

Overall measurement system uncertainty was controlled through precision and accuracy acceptance criteria for field and preparation duplicate samples, although measurement quality objectives were not defined for system-wide detectability. Although the instrument detection limit is an integral part of the detectability issue, the actual detection limit that should be applied to the evaluation of detectability in the routine sample data set is the system detection limit. Less than 80 percent of the Mid-Appalachian routine sample data for exchangeable calcium and sodium in ammonium chloride and ammonium acetate, extractable iron in calcium chloride and acid oxalate, silicon in acid oxalate, and total sulfur parameters is greater than the corresponding system detection limit. *It is recommended that, in addition to instrument detectability, system detectability be addressed in the measurement quality objectives for future surveys.* Although some consideration has been given to the development of a soil blank sample, *it is recommended that low concentration audit samples, entered into the system during the sampling and analytical phases, continue to be used as substitutes for soil blank samples.* These audit samples serve not only to identify contamination and allow the calculation of instrument and system detection limits, but also are used to evaluate system-wide accuracy as well as providing additional quality management benefits at the preparation laboratory. A comparison of low-range field audit samples and low-range laboratory audit samples showed no indication of contamination from any phase of the measurement system.

Considerable effort was expended during the course of the three surveys to evaluate and improve the detectability of various parameters. In particular, significant improvement was obtained for the exchangeable cations and the sulfur parameters. The detection limits used in the surveys have been tightened and refined in conjunction with improvement in analytical methods and instrumentation. However, improvement in detectability is a continuum that should be continually addressed. For similar studies of sensitive ecosystems, *it is recommended that effort be directed towards improving detectability for future surveys.* Additional methods research is essential to this effort. In addition, guidance is needed from the data users concerning the lowest analyte concentrations about which there is concern. This input could lead to a substitution of methods, and could reduce the time and effort expended in assuring the quality of measured values at low concentrations that are not of major concern.

Precision

The precision results indicate that the analytical within-batch precision objectives were satisfied in most cases. This shows that the measurement quality objectives were well-designed and appropriate to satisfy the goals of the DDRP. Occasionally an objective was not satisfied for an upper or lower tier of a parameter, such as magnesium in calcium chloride or silicon in acid oxalate. The laboratories might have had difficulty in satisfying certain precision objectives, e.g., an objective might be unreasonably restrictive or the laboratories might have had problems with the analytical method or sample homogenization. Another possibility was that the inordinate effect of outlying data points was responsible for a large portion of the unsatisfactory precision. Other parameters, however, showed better than expected precision. *It is recommended that the lower tier precision objective be lowered from 0.20 to 0.10 milliequivalents per 100 grams and the upper tier precision objective be lowered from 15 to 10 percent relative standard deviation for exchangeable aluminum in ammonium chloride (AL_CL). It is recommended that the data users consider increasing the upper tier precision objective from 10 to 15 percent relative standard deviation for extractable silicon in acid oxalate (SI_AO).*

Increasing sources of confounded data collection error led to increased standard deviations in the precision estimates. However, the precision of the duplicate samples prepared by the preparation laboratory was about the same, on average, as the laboratory audit samples which did not undergo any additional subsampling. This indicates that the preparation laboratory performed very well in subsampling the bulk soil samples. In many cases, the error estimates for the preparation duplicates were less than that for the audit samples. It is possible that the quality assurance staff had more difficulty in homogenizing the 500-kilogram bulk audit samples compared to the 5-kilogram routine samples homogenized at the preparation laboratory. The audit samples were homogenized and subsampled using a modified cone-and-quartering technique (Schumacher et al., in review) and the preparation duplicates were homogenized and subsampled with five passes through a closed-bin riffle splitter. This difference has implications for the preparation of audit samples, i.e., the need for a more standardized homogenization method. *It is recommended that the future preparation of audit samples utilize a large closed-bin riffle splitter during the subsampling procedure.*

For the field duplicates, precision objectives were exceeded for only a few parameters, usually because of the inordinate effect of one or two field duplicate/routine pairs. In addition, the high precision for the field duplicates for some parameter groups suggests that the component of error from soil sampling is not a large portion of the data collection error. *It is recommended that a review be made of the measurement quality objectives for field sampling and sample preparation because of the lower than expected variability in these two measurement phases.* The sampling class/horizon groups showed the greatest variability due to the inherent population variability in the routine samples.

Pooling the precision estimates for each parameter into parameter groups allowed the within-batch components of precision to be evaluated with respect to the ability of the laboratories to achieve the precision objectives. Table 4-1 is a summary of the overall achievement of the measurement quality objectives for analytical within-batch precision for 42 of the 50 parameters arranged into parameter groups. A precision index was determined for each group of parameters by pooling and weighting the parameter standard deviations for each of the lower and upper tiers, where appropriate, and dividing by the respective measurement quality objective for each tier. These values were then pooled and weighted across the two tiers for the group. A precision index less than 1.0 indicates that the precision estimate for this parameter group satisfied the "overall objective" when viewed from the perspective of the entire concentration range, where a lower precision index denotes higher precision. A precision index of 1.0 or higher would indicate that the parameter group did not satisfy the overall objective. This approach helped to identify which parameter groups might require further quality assurance emphasis in order to redefine the objectives for future surveys or to reassess the analytical

Table 4-1. Precision Indices for Parameter Groups Based on Pooled Within-Batch Estimates

Parameter group (parameters included)	Precision index*
Particle size analysis (SAND, SILT, CLAY)	0.52
Soil pH (PH_: H2O, 002M, 01M)	0.45
Cations in ammonium chloride (CA, MG, K, NA: _CL)	0.52
Cations in ammonium acetate (CA, MG, K, NA: _OAC)	0.48
Cation exchange capacity (CEC_CL, CEC_OAC)	0.58
Exchangable acidity (AC_BACL)	0.41
Cations in calcium chloride (CA, MG, K, MG, FE, AL: _CL2)	0.32
Extractable iron and aluminum (FE_, AL_: PYP, AO, CD)	0.46
Extractable sulfate (SO4_: H20, PO4)	0.90
Sulfate isotherms (SO4_: 0 - 32)	0.58
Total elemental analysis (C_TOT, N_TOT, S_TOT)	0.62

[*] Critical index = 1.00; values exceeding this level are considered unsatisfactory so far as achievement of measurement quality objectives is concerned.

procedures for the affected parameters. All precision indices were less than 1.0, which suggests that overall precision was very [illegible] in relation to the survey objectives.

Accuracy

Accuracy in the Mid-Appalachian survey was evaluated by quantitatively estimating analytical bias with respect to a reference value, defined as the central tendency of an accuracy window for a given parameter. Laboratory differences and trends were assessed by comparing mean parameter values for the laboratories, combined across audit samples, to their respective reference values.

Analytical bias estimates were pooled from each parameter into appropriate parameter groups to assess laboratory performance as a function of analytical methodology. Table 4-2 shows the analytical bias in relation to the system detection limit for the chemical parameters arranged into parameter groups. An accuracy index was determined for each group of parameters by averaging the bias values for all parameters within a group and dividing by the average system detection limit for the group. Accuracy indices less than 1.0 show that the bias for the parameter group was less than the system detection limit for the parameter group, signifying negligible bias in the sample analysis. Accuracy indices of 1.0 and higher show the presence of significant laboratory bias. The system detection limit was used as the basis for comparison with bias because it represents the detection limit for all phases of the measurement system including field sampling, sample preparation, and sample analysis. No measurement quality objectives for bias were established, therefore, no overall achievement of bias objectives could be estimated.

Table 4-2. Accuracy Indices for Parameter Groups Based on Pooled Bias Estimates

Parameter group (parameters included)	Accuracy index*
Cations in ammonium chloride (CA, MG, K, NA : _CL)	0.04
Cations in ammonium chloride (CA, MG, K, NA : _OAC)	0.10
Cation exchange capacity (CEC_CL, CEC_OAC)	0.45
Exchangeable Acidity (AC_BACL)	0.04
Cations in calcium chloride (CA, MG, K, NA, FE, AL : _CL2)	0.26
Extractable iron and aluminum FE_, AL_: PYP, AO, CD)	0.12
Extractable sulfate (SO4_H2O, SO4_PO4)	0.36
Sulfate isotherm (SO4_0)	0.12
Total elemental analysis (C_TOT, N_TOT, S_TOT)	0.50

[*] Critical index = 1.00; values exceeding this level are considered to show significant bias.

The accuracy indices assist in identifying which parameter groups should undergo further quality assurance emphasis and can be helpful in defining and establishing measurement quality objectives for bias in future soil surveys. All accuracy indices were considerably below 1.0 for the Mid-Appalachian survey, which suggests that bias was negligible when viewed from this system-wide perspective.

As a summary assessment of laboratory differences, the average deviation from the reference value was estimated, using multivariate analysis, for each laboratory (L1, L2, and L4) across audit samples and parameters within each parameter group. The ratio of the squared deviation to the variance of the prior reference distribution was evaluated across audit samples and parameters within each parameter group. Significance of the differences is expressed as an index for each parameter group, where an index of 1.0 or higher denotes a significant laboratory difference (see Table 4-3). None of the laboratories were significantly different from the variance of the prior reference distribution for any parameter group. The similarity in the indices among laboratories for a given parameter indicates that there was similarity in laboratory performance.

Quality is a continuum and the need for a specific level of data quality dictates the measurement quality objectives. These objectives may or may not be attainable with the current technology. The analytical procedures for the methods should be examined for their ability to accomplish the analysis at the level specified. No single laboratory was consistently superior to the others for all parameters or parameter groups. Each laboratory appears to have individual strengths in specific analytical methods, which is probably a reflection of the combination of experience, instrumentation, and laboratory management within each laboratory. This resulted in a patchwork of differences on a parameter group basis. In order to control interlaboratory differences in future surveys, *it is recommended to continue the selection of a specific laboratory to perform analyses on a parameter basis for those parameters which use specialized instrumentation, e.g., total elemental analysis (C_TOT, N_TOT, S_TOT).*

Table 4-3. Laboratory Difference Indices for Parameter Based on Pooled Deviations from Reference Values

Parameter group	Laboratory difference index[*]		
	L1	L2	L4
Particle size analysis (SAND, SILT, CLAY)	0.21	0.39	0.39
Soil pH (PH_: H2O, 002M, 01M)	0.29	0.25	0.44
Cations in ammonium chloride (CA, MG, K, NA: _CL)	0.56	0.20	0.21
Cations in ammonium acetate (CA, MG, K, NA: _OAC)	0.29	0.35	0.23
CEC and exchangeable acidity (CEC_CL, CEC_OAC, AC_BACL)	0.27	0.32	0.35
Cations in calcium chloride (CA, MG, K, MG, FE, AL: _CL2)	0.25	0.19	0.18
Extractable Fe, Al, Si (FE_, AL_: PYP, AO, CD; SI_AO)	0.36	0.30	0.24
Extractable sulfate (SO4_: H20, PO4)	0.60	0.35	0.23
Isotherms (SO4_: 0 - 32)	0.25	0.27	0.38

[*] Critical index = 1.00; laboratories exceeding this level are considered to show significant deviation from the reference value.

One of the major goals of any quality assurance program is to reduce the occurrence of both random and systematic errors, hence, selection of the best possible laboratories is of primary importance. As shown in previous DDRP surveys, analytical performance among laboratories varies widely and, as demonstrated for analyses in this and previous DDRP reports, laboratories can differ substantially in their performance for certain parameters. *It is recommended that a stringent performance evaluation process be continued to select qualified contract analytical laboratories.*

Successful quality control of a measurement process results in statistical control of the resulting data. With this in mind, a quality control soil audit sample was successfully incorporated into the quality assurance program and allowed the laboratories to monitor the accuracy of the batch analysis. Laboratories were provided with a range of acceptable analyte concentrations for this sample and, for each sample batch, the laboratories were required for all analyses to satisfy contractually-defined accuracy criteria on a batch-by-batch basis. If the reported analytical results were not within the designated accuracy windows, the laboratory was required to reanalyze a batch of samples until the reported audit sample values satisfied the acceptance criteria. This procedure ensured that each laboratory could meet a rigid standard for each batch of samples analyzed prior to final submission of the analytical results. Between-batch uncertainty and laboratory differences were markedly reduced through the use of this sample. *It is recommended that the use of a quality control audit sample be continued in future surveys.*

Data derived from soil analytical methods which determine extractable or exchangeable soil constituents may contain errors stemming from soil extraction as well as from the instrument. The former is assumed to be the main cause of differences among the laboratories and is a major reason for conducting interlaboratory comparison studies. Without the ability to distinguish between extraction and instrument error, however, it is not known whether one or both types of errors are present and where to focus efforts to reduce systematic bias. *It is recommended that liquid audit samples be incorporated into the quality assurance program and be used to differentiate between error resulting from soil extraction and error resulting from instrumentation.*

As a result of information gained in this survey, *it is recommended that the accuracy windows be redefined for future surveys using data from all three DDRP surveys.* It was observed by several DDRP reviewers that quality control charts were not used as consistently nor effectively as possible during the batch analysis. Extensive use of control charts in real time would have improved the ability of the quality assurance staff to detect trends or other differences among the batches. *It is recommended that emphasis be placed on the use of audit sample control charts by the QA staff to identify abnormal scatter or trends outside the accuracy windows during batch analysis.*

Representativeness

In evaluating representativeness of the quality assurance samples, it is evident that the field duplicates and preparation duplicates are representative of the range of concentration in the range of the routine samples for most parameters. *It is recommended that the field sampling and preparation laboratory protocols continue to specify statistically valid methods for selecting the field and preparation duplicates.* The method should be reiterated to the sampling and laboratory personnel during the pre-sampling training session. The sampling crew leaders should ensure that a sufficient amount of soil is collected for each bulk sample during sampling to allow a preparation duplicate to be subsampled.

Completeness

Sampling of the specified pedons had a completeness level of 100 percent, and processing was accomplished for 100 percent of the soil samples satisfying the sample receipt criteria at the preparation laboratory. Analytical completeness in the verified data bases was 100 percent for all parameters. Sufficient validated data were generated to make conclusions for each parameter in the Mid-Appalachian survey data bases.

Comparability

An interlaboratory comparability study has indicated that soils data collected from DDRP analytical methods were comparable to data obtained, using similar methods, from independent laboratories in the United States and Canada. This finding has positive implications for comparability of the DDRP data with other data bases and is especially important considering the large geographical aspects of the DDRP surveys. This comparability aspect is further evidence of the thoroughness of the quality assurance program and the appropriateness of the analytical design to satisfy the requirements of the data users.

Comparability was observed to have several levels of suitability that must be satisfied before multiple sets of data can be directly compared. Numerous differences in data quality objectives existed between the three DDRP surveys, and overall data quality is generally best in the Mid-Appalachian survey.

Therefore, some of the analytical data from the Northeastern and Southern Blue Ridge Province surveys may not be suitable for the same data analysis comparisons as the Mid-Appalachian survey data. In most cases, the sampling, preparation, and analytical methods and protocols for the three surveys were comparable.

General quantitative comparisons of all parameters common to the three surveys were made using the Bw horizon audit samples. Results of an *F* test revealed several parameters with significant differences across surveys. *It is recommended that data users exercise caution when using DDRP analytical data from the following parameters: AL_CL vs. AL_KCL, and SO4_H2O, SO4_O, SO4_4, CA_CL2, COSI, FE_CD, and C_TOT.* Data comparability across the three surveys is generally good, as 40 of the 49 parameters (82 percent) common to the three surveys did not show highly significant differences. *It is recommended that a data comparison be performed between the two soil extraction solutions used for exchangeable aluminum in 1M ammonium chloride (AL_CL) and 1M potassium chloride (AL_KCL).*

Uncertainty Estimation

The step function statistical approach has been shown to be an effective procedure for evaluating measurement quality issues in environmental data spanning a wide range of concentration. *It is recommended that additional research and development be undertaken to identify an optimal step function procedure that is fully compatible with the measurement quality sample design.*

It was determined that measurement uncertainty is negligible for 90 percent (45 of the 50 parameters) of the data. The five exceptions to this finding were the VFS, COSI, NA_CL, NA_OAC, and SI_AO parameters. Additional methods research would identify ways to reduce the contribution of measurement uncertainty in these parameters.

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Glossary

accuracy[6]	the level of agreement between an observed value and the "true" value of a soil characteristic
accuracy window[6]	confidence interval established about the reference value of a given parameter for the purpose of controlling laboratory analytical results on a batch-by-batch basis
acid neutralizing capacity[6]	ability of a soil to buffer or neutralize acid-generating conditions
additive model[6]	statistical model in which the component effects are considered to be additive
aliquot[6]	a subsample of soil taken from a container of homogenized analytical sample
anion[5]	a negatively-charged ion, as one attracted to the anode in electrolysis
anthropogenic[5]	contribution of man-made influences and products to the environment; influenced by man
atmospheric deposition[6]	placement of natural and unnatural substances into the ecosystem through wet and dry fall processes
autocorrelation[6]	correlation among sequential observations
average deviation[6]	the average distance in reporting units, without regard to sign, from the reference value
base saturation[6]	degree or percent of the total cation holding capacity of a soil that is occupied by base cations, mainly calcium, magnesium, potassium, and sodium
between-batch[6]	the effect of soil samples entering the laboratories in separate batches of samples and analyzed on different days

(continued)

Glossary *(continued)*

bias[6]	systematic and/or random error, with respect to a reference value, inherent in a method and normally caused by some artifact or idiosyncrasy of the measurement system, e.g., temperature effects, extraction inefficiencies, mechanical losses, and calibration errors; bias may have a positive or negative sign, and several kinds of bias can exist concurrently
blind sample[1]	a sample submitted for analysis whose composition is known to the submitter but is unknown to the analyst; a blind sample is one way to test proficiency of a measurement process
cation[5]	a positively-charged ion, or one attracted to the cathode in electrolysis
cation pool[6]	differing level of availability of soil cations which are extracted by varying the ionic strength of the extracting solutions
comparability[6]	the similarity of data from different sources included in a given set of data and the similarity of methodologies from related projects across the regions of interest
completeness[6]	the quantity of data that is successfully collected with respect to the amount intended in the experimental design
concentration dependency[6]	refers to the increasing variability of soil analytical data with increasing concentration for some soil parameters
confounded[6]	intermingled in such a way as to be inseparable
contract-required detection limit[6]	instrument detectability criterion established for each parameter in contractual agreement with a laboratory
control chart[1]	a graphical plot of test results with respect to time or sequence of measurement together with limits within which they are expected to lie when the system is in a state of statistical control
data qualifier[6]	annotation, or flag, applied to a datum and denoting to a possible data quality discrepancy
data quality objective[6]	user-defined criteria established for each parameter to evaluate useability of the data
delta value[6]	an estimate of uncertainty generated from a data set and used to evaluate the contribution of uncertainty to a specified data value

(continued)

Glossary *(continued)*

detectability[6]	the determination of the low-range critical value of a soil characteristic that a method-specific procedure can reliably discern
double-blind sample[1]	a sample known by the submitter but submitted to the analyst in such a way that neither its composition nor its identification as a check sample are known
endogenous[5]	originating from within; the natural composition of a soil
extraction[6]	removal of soil constituents by agitation (mixing, shaking, replacement) of soil analytes using a solution of known ionic strength and composition
flag[6]	(see "data qualifier")
fragipan[2]	a dense, brittle subsurface horizon that restricts water movement and root penetration
horizon[2]	a layer of soil of varying thickness, approximately parallel to the land surface, that has distinct characteristics produced by soil-forming processes
hydrophilic[6]	water-attracting
hydrophobic[6]	water-repelling
instrument detection limit[3]	three times the standard deviation of ten nonconsecutive replicate calibration blank analyses run on separate days; or, if a signal is not obtained, three times the standard deviation of 10 nonconsecutive replicate analyses of a standard whose concentration is four times the lesser of the actual detection limit or the contract required detection limit
invitation for bid[6]	a document provided to a potential contractor for solicitation in order to estimate procedures, costs, and intention for performing an analytical service
knot[6]	a point within the concentration range separating the data evaluated by absolute and relative measures of precision
laboratory difference[6]	the variation between the mean of repeated measurements for a given laboratory and the reference value for a given parameter
linear dynamic range[6]	the range of analyte concentration for which the calibration curve is approximately a straight line

(continued)

Glossary (continued)

logistics[5]	relates to the procurement, maintenance, and movement of equipment, supplies, or personnel
measurement quality objective[6]	critical level which, if exceeded, is considered to append additional, and possibly unacceptable, measurement uncertainty to the corresponding data
measurement quality samples[6]	quality evaluation or quality control samples which are placed in each batch of soil samples for assessment purposes
measurement uncertainty[6]	based on delta values calculated from audit samples, preparation duplicate samples, and field duplicate samples which contain various configurations of sampling, preparation, and analytical uncertainty
mineral soil sample[4]	a soil sample consisting predominantly of, and having its properties determined predominantly by, mineral matter; usually contains < 20% (by weight) organic matter
multivariate analysis[6]	analysis in which more than one variable is considered simultaneously
organic soil sample[4]	a soil sample which contains 20 percent or more (by weight) organic matter
outlier[1]	a value which appears to deviate markedly from that of other members of the population in which it occurs
overall data uncertainty[6]	confounded population and measurement uncertainty in the sampling class/horizon groups of routine samples
pedon[6]	a three-dimensional body of soil having lateral dimensions large enough (1 to 10 square meters in area) to permit the identification and sampling of its soil horizons
performance evaluation[6]	assessment of laboratory capability to perform an analytical service by conducting and evaluating overall results of an analytical solicitation and preliminary analysis
precision[6]	the level of agreement among multiple measurements of a soil characteristic
QART[6]	quality assurance reanalysis template used during data verification to make decisions relating to the batch acceptance criteria
quadrature[6]	the square root of the pooled variance and squared bias terms used to evaluate data uncertainties

(continued)

Glossary (continued)

quality assurance[1]	a system of activities whose purpose is to provide to the producer or user of a product or a service the assurance that it meets defined standards of quality; consists of two separate but related activities, quality control and quality evaluation
quality control sample[6]	any sample utilized by the analyst to check immediate instrument calibration or response, whose measurement is expected to fall within specific acceptance criteria or control limits
quality evaluation sample[6]	double-blind sample placed among routine test samples for the purpose of assessing and, possibly, controlling the quality of analytical data produced
representativeness[6]	the degree to which the data collected accurately represent the population of interest
sesquioxides[3]	generally considered to be iron and aluminum oxides; more specifically, sesquioxides are combinations of these two minerals in a one-to-one ratio
soil chemistry relationship[4]	a quantitative empirical relationship between two or more soil chemical variables that is assumed to be valid for most soils
step function[6]	a function which takes stationary values within different segments of its domain; used to partition the routine soil data into intervals to assess measurement uncertainty issues
system detection limit[6]	for each chemical variable, except pH, a value calculated from low-range field audit sample data indicating the critical concentration of analyte measured in a routine sample that is detectable and distinguishable from background noise or contamination
uncertainty[6]	a measure of imprecision, bias, or other sources of variability in a given value
validation[3]	the process of determining the legitimacy of data, involving internal consistency checks for outlier removal and definition of levels of confidence
variability[6]	imprecision about a specific characteristic

(continued)

Glossary *(continued)*

verification[3]	the process of confirming the integrity of data, involving discrepancy checks and precision accuracy evaluations
within-batch[6]	the effect of soil samples entering the laboratories in separate batches of samples

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[1] Taylor, 1987
[2] Soil Glossary
[3] QA Soils Definitions
[4] Glossary of Soil Science Terms
[5] Random House College Dictionary
[6] Text

Appendix A

Analytical Data Verification and Validation Flags

This appendix lists the data qualifiers, or flags, that are assigned to the verified and validated data bases. The verification flags specify the nature of discrepancies on a batch and sample basis, while the validation flags are used to characterize more general types of discrepancies that may affect the level of confidence applied to each datum in the validated data base. The verification flags are applied only to the analytical laboratory data and are unrelated to similarly-defined flags used for the preparation laboratory data.

Table A-1. Analytical Data Verification Flags

Blank Exception Program	
B4**	Potential negative sample bias based on laboratory blank data.
B5**	Mean of reagent blanks is > CRDL.
B6*	Laboratory calibration blank is > CRDL.
B9**	Insufficient number of calibration blanks were run.
Replicate Precision Exception Program	
D1**	Analytical duplicate (AD/routine) precision is > maximum expected SD or %RSD.
D5**	Preparation duplicate (PDF/FD) precision is > maximum expected SD or %RSD.
D6**	Preparation duplicate (PDF/routine) precision is > maximum expected SD or %RSD.
D7**	Field audit pair/triplicate (FAP/FAO) precision is > maximum expected SD or %RSD.
D8**	Laboratory audit pair/triplicate (LAP/LAO) precision is > maximum expected SD or %RSD.
D9**	Field duplicate (FD/routine) precision is > maximum expected SD or %RSD.
Detection Limit Exception Program	
L1**	Instrument detection limit (IDL) is > contract-required detection limit (CRDL).
Audit Accuracy Program	
N0**	Low-range laboratory audit (LAL) sample value is > upper accuracy limit.
N1**	LAL sample is < lower accuracy limit.
N2**	Mean of LAP or LAO is > upper accuracy limit.
N3**	Mean of LAP or LAO is < lower accuracy limit.
N4**	Quality control audit sample (QCAS) is > upper accuracy limit.
N5**	QCAS is < lower accuracy limit.
QCCS Exception Program	
Q1**	Quality control check sample (QCCS) is > upper control limit.
Q2**	QCCS is < lower control limit.
Q3**	Insufficient quantity of QCCS were measured.
Q4**	Detection limit QCCS is not within 20% of the theoretical concentration.
Spike Program	
S1**	Percent recovery of matrix spike is above contractual criteria (>105% for sulfate isotherm parameters, >110% for all other sulfate parameters).
S2**	Percent recovery of matrix spike is below contractual criteria (<95% for sulfate isotherm parameters, <90% for all other sulfate parameters).
S3**	Spike solution readings are outside of contractual criteria (sulfate isotherm and extractable calcium parameters only).

(Continued)

Table A-1. Continued

Miscellaneous	
AO*	Value missing
MO*	Value was obtained by using a method that is unacceptable according to the contract.
WO*	Air-dry sample weight is not within contractual requirement.
W2*	Sample extract volume is not within contractual requirement.
XO*	Invalid but confirmed data based on review of QE/QC data.
X1*	Invalid but confirmed data: potential gross contamination of sample or parameter.
X2*	Invalid but confirmed data: potential gross contamination of pedon.
X3*	Possible contamination due to either sampling technique, e.g., bucket augering, or soil amendments, e.g. herbicides, liming, manure, etc.
X4*	Outliers from statistical internal consistency check; raw data and reported data checked only for transcription errors.
X5*	Outliers from manual pedon/horizon internal consistency check; raw data and reported data checked only for transcription errors.
Soil Chemistry Relationships	
C1*	PH_H20 < PH_002M if pH differences > 0.05 units.
C2*	PH_002M < PH_01M if pH differences > 0.05 units.
C3*	PH_H20 < PH_01M if pH differences > 0.05 units.
C4*	CEC_OAC < CEC_CL if CEC_CL > 1 meq/100g and PH_H2O < 7.0
C5*	CA_OAC + MG_OAC + K_OAC + NA_OAC > CEC_OAC if CEC_CL > 1 meq/100g
C6*	CA_CL + MG_CL + K_CL + NA_CL > CEC_CL if CEC_CL > 1 meq/100g
C7*	CEC_OAC/CLAY > 50 if CLAY > 1.0% and CEC_CL > 1 meq/100g
C8*	CEC_CL/CLAY > 50 if CLAY > 1.0% and CEC_CL > 1 meq/100g
C9*	AL_CL > 0.01 meq/100g if PH_H2O > 6.0
H1*	NA_CL2 > NA_CL * 1.10 if NA_CL2 > 0.03 meq/100g.
H2*	K_CL2 > K_CL * 1.10 if K_CL2 > 0.003 meq/100g.
H3*	MG_CL2 > MG_CL * 1.10 if MG_CL2 > 0.008 meq/100g.
I1*	SO4_32 < SO4_16 if SO4_32N ≤ 7.5 mg S/kg soil.
I2*	SO4_16 < SO4_8 if SO4_32N ≤ 7.5 mg S/kg soil.
I3*	SO4_8 < SO4_4 if SO4_32N ≤ 7.5 mg S/kg soil.
I4*	SO4_4 < SO4_2 if SO4_32N ≤ 7.5 mg S/kg soil.
I5*	SO4_2 < SO4_0 if SO4_32N ≤ 7.5 mg S/kg soil.
I6*	SO4_32N < SO4_16N if SO4_32N ≥ 7.5 mg S/kg soil.
I7*	SO4_16N < SO4_8N if SO4_32N ≥ 7.5 mg S/kg soil.

(Continued)

Table A-1. Continued

I8*	SO4_8N < SO4_4N if SO4_32N ≥ 7.5 mg S/kg soil.
I9*	SO4_4N < SO4_2N if SO4_32N ≥ 7.5 mg S/kg soil.
I0*	SO4_2N < SO4_0N if SO4_32N ≥ 7.5 mg S/kg soil.
NC*	Not checked because basic initial criteria were not met.
R1*	SO4_H2O > SO4_PO4 if SO4_PO4 > 1 mg S/kg soil (mineral samples); SO4_H2O > SO4_PO4 * 1.10 (organic samples).
R2*	SO4_H2O/SO4_0 < 4 or > 20 if SO4_H2O ≥ 2 mg S/kg and SO4_0 ≥ 0.1 mg S/kg.
T1*	C_TOT/S_TOT < 7 or > 50 if C_TOT ≥ 0.1% and S_TOT ≥ 0.005%.
T2*	C_TOT/N_TOT < 40 or > 400 if C_TOT ≥ 0.1% and N_TOT ≥ 0.03%.

* Sample Flag: flags the affected parameter for specified samples only.
** Batch-wide Flag: flags the affected parameter for all samples in the batch (assumes that measurement quality samples are representative for the batch).

Table A-2. Analytical Data Validation Flags

Interquartile Outlier Program

L1	Value is < Q_1 - 1.5xIQR but >Q_1 - 3xIQR
L3	Value is < Q_1 - 3xIQR
U1	Value is > Q_3 + 1.5xIQR but <Q_3 + 3xIQR
U3	Value is > Q_3 + 3xIQR

Outlier Validation Program

V1	Datum has verification flag type K, W, M, or X
V2	QE/QC data outside expected ranges
V3*	Horizon aggregation problem
V4	Misclassification in sampling class
V5*	Field data notes indicate possible contamination in the pedon
V6	X4 or X5 verification flag present
V7**	Double check for use in aggregating
V8**	Internally inconsistent chemistry
V9**	Indeterminate problem or negative value
DH	Impossible value for parameter

Internal Consistency Program

VD	PH_01M ≤ 6.5 and 2 ≤ CEC_OAC < CEC_CL
VF	(0.75 * CEC_CL) < SBC_CL if PH_01M ≤ 6.5 and 2 ≤ CEC_CL; (0.75 * CEC_OAC) < SBC_OAC if PH_01M ≤ 6.5 and 2 ≤ CEC_CL
VH	CA_OAC < MG_OAC; CA_OAC < NA_OAC; CA_OAC < K_OAC; CA_CL < MG_CL; CA_CL < NA_CL; CA_CL < K_CL; CA_CL2 < MG_CL2; CA_CL2 < NA_CL2; CA_CL2 < K_CL2
VJ	PH_01M < 3 and BS_CL > 10%
VK	PH_01M < 3 and BS_OAC > 7%
VL	PH_01M > 6 and BS_CL < 50%
VM	PH_01M > 6 and BS_OAC < 40%
VP	(CEC_OAC / CEC_CL) < 1.5 if CEC_OAC and CEC_CL ≥ 2 meq/100g and PH_01M < 6.0
VQ	AL_AO < AL_CD; FE_CD < FE_AO; (AL_AO + FE_AO) < (AL_PYP + FE_PYP); (AL_CD + FE_CD) < (AL_PYP + FE_PYP);
VW	(S_TOT * 1000) < SO4_PO4 if S_TOT ≥ 0.01% (organic soils)
VX	(S_TOT * 2000) < SO4_PO4 if S_TOT ≥ 0.01% (organic soils)
VY	(S_TOT * 10000) < SO4_PO4 if S_TOT ≥ 0.01% (mineral soils)
VZ	(S_TOT * 5000) < SO4_PO4 if S_TOT ≥ 0.01% (mineral soils)

(Continued)

Table A-2. Continued

HB	MG_OAC < MG_CL2 if MG_CL2 ≥ 0.05 meq/100 g
HE	CEC_CL < AL_CL2 if AL_CL2 ≥ 0.05 meq/100 g
HG	(CA_CL + 0.8) < CA_CL2
HI	CA_OAC < 0 meq/100 g; MG_OAC < 0 meq/100 g; NA_OAC < 0 meq/100 g; K_OAC < 0 meq/100 g; CA_CL < 0 meq/100 g; MG_CL < 0 meq/100 g; NA_CL < 0 meq/100 g; K_CL < 0 meq/100 g; CA_CL2 < 0 meq/100 g; MG_CL2 < 0 meq/100 g; NA_CL2 < 0 meq/100 g; K_CL2 < 0 meq/100 g; AL_CL2 < 0 meq/100 g; FE_CL2 < 0 meq/100 g
HJ	(((CA_CL2 + MG_CL2 + NA_CL2 + K_CL2 + FE_CL2 + AL_CL2) * 5000) - (ΣSO4_0-32) * 125) - 4000) / 4000 > 2
HK	(((CA_CL2 + MG_CL2 + NA_CL2 + K_CL2 + FE_CL2 + AL_CL2) * 5000) - (ΣSO4_0-32) * 125) - 4000) / 4000 < -0.5

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* Sample Flag: flags the affected parameter for specified samples only.

** Batch-wide Flag: flags the affected parameter for all samples in the batch (assumes that measurement quality samples are representative for the batch).

Appendix B

Quality Assurance Reanalysis Templates

The following QARTs are used in the evaluation of QE/QC and routine sample data. As a batch of soils data is received, it is reviewed according to the criteria set forth in the template. If major uncertainty or a large occurrence of minor uncertainty is identified, confirmation or reanalysis is requested for the affected parameter and batch.

SAND, SILT

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > 3.0 if value at lower limit 2) prep dup/field dup pair: SD > 3.0 if value at lower limit 3) mean value lab audits out of accuracy window, or SD > 3.0 if value at lower limit 4) low level lab audit out of accuracy window	If 1 out of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > 6.0 if value at lower limit	Within batch precision: SD < 6.0 if valur at lower limit
Soil Chemistry Relationships	NONE	NONE	NONE
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-1. Quality assurance reanalysis template for the determination of SAND and SILT.

CLAY

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of the 4 relationships occur: 1) prep dup/routine pair: SD > 2.0 if value at lower limit 2) prep dup/field dup pair: SD > 2.0 if value at lower limit 3) mean value lab audits out of accuracy window, or SD > 2.0 if value at lower limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > 4.0 if value at lower limit	Within batch precision: SD < 4.0 if value at lower limit
Soil Chemistry Relationships	If any relationship occurs ≥ 6 times: CEC_OAC/CLAY > 50 if clay > 1.0 and CEC_CL > 1 meq/100 g CEC_CL/CLAY > 50 if clay > 1.0 and CEC_CL > 1 meq/100 g	If relationships occur < 6 times	If relationships do not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-2. Quality assurance reanalysis template for the determination of CLAY.

PH_H20, PH_OO2M, PH_01M

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > 0.1 if value at lower limit 2) prep dup/field dup pair: SD > 0.1 if value at lower limit 3) mean value lab audits out of accuracy window, or SD > 0.1 if value at lower limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > 0.2 if value at lower limit	Within batch precision: SD < 0.2 if value at lower limit
Soil Chemistry Relationships	If relationship occurs ≥ 6 times PH_H20 < PH_002M < PH_01M if difference > .05	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-3. Quality assurance reanalysis template for the determination of PH_H20, PH_002M, and PH_01M.

CA, MG, NA, K_CL, CA, MG, NA, K_OAC

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .02 if value at lower limit %RSD > 15% if value at upper limit 2) prep dup/field dup pair: SD > .02 if value at lower limit %RSD > 15% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > .02 if value at lower limit %RSD > 10% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	none	Within batch precision: SD > .04 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD < .04 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	If relationships occur ≥ 6 times: CA_OAC + MG_OAC + NA_OAC + K_OAC > CEC_OAC if CEC_CL > 1 meq/100 g CA_CL + MG_CL + NA_CL + K_CL > CEC_CL if CEC_CL > 1 meq/100 g	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-4. Quality assurance reanalysis template for the determination of CA, MG, K, NA_CL, and CA, MG, K, NA_OAC.

AL_CL

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .20 if value at lower limit %RSD > 22% if value at upper limit 2) prep dup/field dup pair: SD > .20 if value at lower limit %RSD > 22% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > .20 if value at lower limit %RSD > 15% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > 5.0 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD < 5.0 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	If relationship occurs ≥ 6 times: AL_CL > 0.1 meq/100 g if pH_H2O > 6.0	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-5. Quality assurance reanalysis template for the determination of AL_CL.

CEC_OAC, CEC_CL

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .25 if value at lower limit %RSD > 15% if value at upper limit 2) prep dup/field dup pair: SD > .25 if value at lower limit %RSD > 15% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > .25 if value at lower limit %RSD > 10% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .50 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD < .50 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	If relationship occurs ≥ 6 times CEC_OAC < CEC_CL if CEC_CL > 1 meq/100 g and PH_H2O < 7.0	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-6. Quality assurance reanalysis template for the determination of CEC_CL and CEC_OAC.

AC_BACL

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > 1.0 if value at lower limit %RSD > 22% if value at upper limit 2) prep dup/field dup pair: SD > 1.0 if value at lower limit %RSD > 22% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > 1.0 if value at lower limit %RSD > 15% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > 2.0 if value at lower limit %RSD > 45% when using upper limit	Within batch precision: SD < 2.0 when using lower limit %SDR < 45% when using upper limit
Soil Chemistry Relationships	NONE	NONE	NONE
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-7. Quality assurance reanalysis template for the determination of AC_BACL

CA_CL2

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .05 if value at lower limit %RSD > 8% if value at upper limit 2) prep dup/field dup pair: SD > .05 if value at lower limit %RSD > 8% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > .05 if value at lower limit %RSD > 5% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 or the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .10 if value at lower limit %RSD > 15% if value at upper limit	Within batch precision: SD < .10 if value at lower limit %RSD < 15% if value at upper limit
Soil Chemistry Relationships	NONE	NONE	NONE
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-8. Quality assurance reanalysis template for the determination of CA_CL2.

MG_CL2, NA_CL2, K_CL2

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD >.005 if value at lower limit %RSD > 15% if value at upper limit 2)prep dup/field dup pair: SD >.005 if value at lower limit %RSD > 15% if value at upper limit 3) mean value lab audits out of accuracy window, or SD >.005 if value at lower limit %RSD > 10% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .010 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD < .010 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	If relationship occurs ≥ 6 times MG_CL2 > MG_CL * 1.10 if MG_CL2 > 10 * CRDL NA_CL2 > NA_CL * 1.10 if NA_CL2 > 10 * CRDL K_CL2 > K_CL * 1.10 if K_CL2 > 10 * CRDL	If relationships occur < 6 times	If relationships do not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-9. Quality assurance reanalysis template for the determination of MG_CL2, K_CL2, and NA_CL2.

FE_CL2

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .01 if value at lower limit %RSD > 22% if value at upper limit 2) prep dup/field dup pair: SD > .01 if value at lower limit %RSD > 22% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > .01 if value at lower limit %RSD > 15% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .02 if value at lower limit %RSD > 45% if value at upper limit	Within batch precision: SD < .02 if value at lower limit %RSD < 45% if value at upper limit
Soil Chemistry Relationships	NONE	NONE	NONE
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-10. Quality assurance reanalysis template for the determination of FE_CL2.

AL_CL2

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .05 if value at lower limit %RSD > 22% if value at upper limit 2) prep dup/field dup pair: SD > .05 if value at lower limit %RSD > 22% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > .05 if value at lower limit %RSD > 15% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .10 if value at lower limit %RSD > 45% if value at upper limit	Within batch precision: SD < .10 if value at lower limit %RSD < 45% if value at upper limit
Soil Chemistry Relationships	NONE	NONE	NONE
Internal Relationships	> 10 outliers	5 - 10 outliers	> 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-11. Quality assurance reanalysis template for the determination of AL_CL2.

FE_PYP, AL_PYP, FE_AO, AL_AO, SI_AO, FE_CD, AL_CD

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .03 if value at lower limit %RSD > 15% if value at upper limit 2) prep dup/field dup pair: SD > .03 if value at lower limit %RSD > 15% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > .03 if value at lower limit %RSD > 10% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .06 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD < .06 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	NONE	NONE	NONE
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-12. Quality assurance reanalysis template for the determination of FE_PYP, AL_PYP, FE_AO, AL_AO, SI_AO, FE_CD, and AL_CD.

SO4_PO4, SO4_H2O

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > 1.5 if value at lower limit %RSD > 15% if value at upper limit 2) prep dup/field dup pair: SD > 1.5 if value at lower limit %RSD > 15% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > 1.5 if value at lower limit %RSD > 5% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > 3.0 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD < 3.0 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	If relationship occurs ≥ 6 times SO4_PO4 < SO4_H2O if SO4_H2O > 1 mg S/kg soil SO4_H2O/SO4_0 > 4 or SO4_H2O/SO4_0 > 20 if SO4_H2O ≥ 2 mg S/kg and SO4_0 ≥ .1 mg S/kg	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-13. Quality assurance reanalysis template for the determination of SO4_PO4 and SO4_H2O.

SO4_0-32

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .10 if value at lower limit %RSD > 8% if value at upper limit 2) prep dup/field dup pair: SD > .10 if value at lower limit %RSD > 8% if value at lower limit 3) mean value lab audits out of accuracy window, or SD > .10 if value at lower limit %RSD > 5% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occur	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .20 if value at lower limit %RSD > 15% if value at upper limit	Within batch precision: SD < .20 if value at lower limit %RSD < 15% if value at upper limit
Soil Chemistry Relationships	If relationship occurs ≥ 6 times SO4_32 < SO4_16 < SO4_8 < SO4_4 < SO4_2 < SO4_0 If SO4_32H >= 7.5 mg S/Kg soil	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-14. Quality assurance reanalysis template for the determination of SO4_0-32.

C_TOT

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD > .05 if value at lower limit %RSD > 15% if value at upper limit 2) prep dup/field dup pair: SD > .05 if value at lower limit %RSD > 15% if value at upper limit 3) mean value lab audits out of accuracy window, or SD > .05 if value at lower limit %RSD > 10% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .10 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD < .10 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	If any relationship occurs $\geq$ 6 times C_TOT/N_TOT < 7 or C_TOT/N_TOT > 50 if N_TOT $\geq$ .03 wt% and C_TOT $\geq$ .1 wt% C_TOT/S_TOT < 40 or C_TOT/S_TOT > 400 if S_TOT $\geq$ .005 wt% and C_TOT $\geq$ .1 wt%	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-15. Quality assurance reanalysis template for the determination of C_TOT.

N_TOT

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD >.015 if value at lower limit %RSD > 15% if value at upper limit 2) prep dup/field dup pair: SD >.015 if value at lower limit %RSD > 15% if value at upper limit 3) mean value lab audits out of accuracy window, or SD >.015 if value at lower limit %RSD > 10% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .03 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD < .03 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	If relationship occurs ≥ 6 times C_TOT/N_TOT < 7 or C_TOT/N_TOT > 50 if N_TOT ≥ .03 wt% and C_TOT ≥ .1 wt%	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-16. Quality assurance reanalysis template for the determination of N_TOT.

S_TOT

	MAJOR	MINOR	NON
Lab Audits & Prep Dups	If any 2 of 4 relationships occur: 1) prep dup/routine pair: SD >.002 if value at lower limit %RSD > 15% if value at upper limit 2) prep dup/field dup pair: SD >.002 if value at lower limit %RSD > 15% if value at upper limit 3) mean value lab audits out of accuracy window, or SD >.002 if value at lower limit %RSD > 10% if value at upper limit 4) low level lab audit out of accuracy window	If 1 of 4 of the relationships listed in the major column occurs	If 0 of 4 of the relationships listed in the major column occur
Field Dups & Field Audits	NONE	Within batch precision: SD > .004 if value at lower limit %RSD > 30% if value at upper limit	Within batch precision: SD <.004 if value at lower limit %RSD < 30% if value at upper limit
Soil Chemistry Relationships	If relationship occur ≥ 6 times C_TOT/S_TOT < 40 or C_TOT/S_TOT > 400 if S_TOT ≥ .005 wt% and C_TOT ≥ .1 wt%	If relationship occurs < 6 times	If relationship does not occur
Internal Relationships	> 10 outliers	5 - 10 outliers	< 5 outliers

Reanalysis is requested with occurrence of 1 major flag or 3 major flags

Figure B-17. Quality assurance reanalysis template for the determination of S_TOT.

Appendix C

Statistics for Step Function Uncertainty Estimates

This table provides statistical information that supplements the results and discussion for uncertainty estimation found in Section 3. Provided are data relating to the development of delta values, including the within-batch and between-batch standard deviations, bias calculations, and proportions. These data can be used to assess the quality of the routine sample data set on the basis of the quality of the QE sample data sets. The table is sorted by parameter and subsorted by data set.

Table C-1. Table of Statistics for Step Function Uncertainty Estimates

Parameter	Data set[a]	Delta	Interval	Mean	Within-batch		Pairs>MQO		Between-batch	
					df	SD	n	(%)	df	SD
MOIST	LAP	.	0.0-1.0	.	.	.	.	.	23	0.0658
			1.0-12.0	3.77	27	0.2157	5	(18.5)	25	0.1693
			12.0-inf	.	.	.	.	.	.	.
	PD	.	0.0-1.0	0.71	22	0.0685	0	(0.0)		
			1.0-12.0	1.69	32	0.0722	0	(0.0)		
			12.0-inf	.	.	.	.	.	Bias	
	FD	.	0.0-1.0	0.73	11	0.0929	0	(0.0)	.	
			1.0-12.0	1.68	16	0.1295	0	(0.0)		
			12.0-inf	.	.	.	.	.	P (i)	
	S/H	.	0.0-1.0	0.79	130	0.5066			0.216	
			1.0-12.0	1.66	488	0.6837			0.784	
			12.0-inf	.	.	.			.	
SAND	LAP	3.4377	0.0-15.0	.	.	.	.	.	.	.
			15.0-35.0	25.04	14	1.1610	0	(0.0)	13	3.3233
			35.0-70.0	46.89	13	1.1581	0	(0.0)	12	3.2846
			70.0-inf	.	.	.	.	.	25	1.0655
	PD	3.4736	0.0-15.0	10.31	4	0.4650	0	(0.0)		
			15.0-35.0	27.09	12	1.8573	1	(8.3)		
			35.0-70.0	48.62	32	0.9958	1	(3.1)		
			70.0-inf	77.43	6	1.3317	0	(0.0)	Bias	
	FD	4.2475	0.0-15.0	10.42	2	0.8139	0	(0.0)	0.3274	
			15.0-35.0	27.50	6	2.2609	0	(0.0)		
			35.0-70.0	48.54	16	2.9892	1	(6.3)		
			70.0-inf	77.38	3	1.9083	0	(0.0)	P (i)	
	S/H	14.5608	0.0-15.0	5.18	1	10.2530			0.008	
			15.0-35.0	27.78	161	13.8975			0.265	
			35.0-70.0	48.53	441	14.5050			0.698	
			70.0-inf	77.39	15	10.5925			0.029	
VCOS	LAP	1.3902	0.0-5.0	3.13	21	0.9093			30	0.7776
			5.0-20.0	5.65	6	0.9192			19	1.2623
			20.0-inf	.	.	.			.	.
	PD	1.4594	0.0-5.0	2.25	31	0.5337				
			5.0-20.0	8.38	22	1.7718				
			20.0-inf	27.55	1	7.1418			Bias	
	FD	1.4582	0.0-5.0	2.14	15	0.4705			0.4016	
			5.0-20.0	7.89	11	1.8355				
			20.0-inf	26.45	1	8.6974			P (i)	
	S/H	3.8479	0.0-5.0	3.04	377	2.5102			0.632	
			5.0-20.0	7.00	241	5.7595			0.365	
			20.0-inf	.	.	.			.	
COS	LAP	1.5563	0.0-5.0	3.79	14	0.4559			13	0.5213
			5.0-20.0	7.62	13	0.8321			36	1.5445
			20.0-inf	.	.	.			1	5.2326
	PD	1.4941	0.0-5.0	2.72	22	0.3240				
			5.0-20.0	8.09	30	0.6559				
			20.0-inf	26.38	2	3.2898			Bias	
	FD	1.6725	0.0-5.0	2.80	11	0.2763			0.7639	
			5.0-20.0	8.07	15	1.2918				
			20.0-inf	25.55	1	3.1820			P (i)	
	S/H	4.3095	0.0-5.0	3.43	238	2.5386			0.405	
			5.0-20.0	8.04	380	5.1207			0.595	
			20.0-inf	.	.	.			.	

(continued)

Table C-1. Continued

Parameter	Data set*	Delta	Interval	Mean	Within-batch df	Within-batch SD	Pairs>MQO n	Pairs>MQO (%)	Between-batch df	Between-batch SD
MS	LAP	1.3945	0.0-5.0	3.52	14	0.2563			13	0.3154
			5.0-20.0	8.09	13	1.1101			12	0.9018
			20.0-inf	.	.	.			26	1.7526
	PD	1.1487	0.0-5.0	2.92	17	0.2532				
			5.0-20.0	12.14	36	0.5893				
			20.0-inf	21.75	1	0.7778			Bias	
	FD	1.3638	0.0-5.0	3.00	9	0.2427			0.5670	
			5.0-20.0	12.05	17	1.0429				
			20.0-inf	20.55	1	0.9192			P (i)	
	S/H	6.1430	0.0-5.0	3.03	102	2.2566			0.184	
			5.0-20.0	10.60	500	6.7744			0.782	
			20.0-inf	24.97	16	9.9827			0.035	
FS	LAP	2.0833	0.0-5.0	4.10	14	0.2535			13	0.4160
			5.0-30.0	11.67	13	0.8155			17	1.9016
			30.0-inf	.	.	.			20	2.1748
	PD	2.0349	0.0-5.0	2.17	8	0.3182				
			5.0-30.0	14.63	44	0.6163				
			30.0-inf	41.72	2	2.8745			Bias	
	FD	2.1160	0.0-5.0	2.32	4	0.1803			-0.5408	
			5.0-30.0	14.50	22	0.8756				
			30.0-inf	40.00	1	2.4042			P (i)	
	S/H	8.0691	0.0-5.0	3.33	18	3.8382			0.040	
			5.0-30.0	13.92	596	8.0112			0.949	
			30.0-inf	35.97	4	9.0569			0.011	
VFS	LAP	1.9734	0.0-5.0	.	.	.			0	.
			5.0-15.0	11.88	22	0.6829			45	1.6758
			15.0-inf	16.75	5	0.5822			3	1.5091
	PD	1.9869	0.0-5.0	2.62	11	0.2567				
			5.0-15.0	9.35	33	0.7560				
			15.0-inf	15.98	10	1.4064			Bias	
	FD	2.2467	0.0-5.0	2.84	6	0.3096			-0.8096	
			5.0-15.0	10.27	18	1.3666				
			15.0-inf	16.42	3	0.7670			P (i)	
	S/H	5.1678	0.0-5.0	3.26	7	3.1279			0.028	
			5.0-15.0	9.19	586	4.6890			0.921	
			15.0-inf	17.26	25	8.3035			0.051	
SILT	LAP	4.1033	0.0-15.0	.	.	.	.	.	26	1.1879
			15.0-35.0	.	.	.	.	.	.	.
			35.0-60.0	50.15	14	2.1340	2	(14.3)	12	3.4679
			60.0-inf	69.78	13	1.5566	0	(0.0)	12	3.4936
	PD	3.0487	0.0-15.0	9.55	3	1.8462	0	(0.0)		
			15.0-35.0	28.12	15	0.9707	0	(0.0)		
			35.0-60.0	43.57	33	1.1875	2	(6.1)		
			60.0-inf	61.32	3	1.3693	0	(0.0)	Bias	
	FD	3.5094	0.0-15.0	7.50	1	0.9899	0	(0.0)	0.8896	
			15.0-35.0	26.62	7	1.6816	0	(0.0)		
			35.0-60.0	43.32	18	2.2215	1	(5.6)		
			60.0-inf	60.90	1	1.1314	0	(0.0)	P (i)	
	S/H	10.6184	0.0-15.0	13.17	9	8.3393			0.017	
			15.0-35.0	27.85	180	10.4795			0.285	
			35.0-60.0	43.35	427	10.1497			0.690	
			60.0-inf	63.25	2	5.3266			0.008	

(continued)

Table C-1. Continued

Parameter	Data set*	Delta	Interval	Mean	Within-batch df	Within-batch SD	Pairs>MQO n	Pairs>MQO (%)	Between-batch df	Between-batch SD
COSI	LAP	8.2282	0.0-10.0	.	.	.			26	1.2327
			10.0-25.0	22.55	7	7.5647			6	5.1822
			25.0-inf	33.19	20	1.4724			18	2.3383
	PD	4.8094	0.0-10.0	6.83	14	0.8313				
			10.0-25.0	14.21	38	0.8294				
			25.0-inf	28.20	2	2.3162			Bias	
	FD	4.8783	0.0-10.0	6.26	6	0.5664			0.1970	
			10.0-25.0	14.02	20	1.3195				
			25.0-inf	26.80	1	0.5657			P (i)	
	S/H	7.1527	0.0-10.0	7.68	69	4.8829			0.116	
			10.0-25.0	13.91	548	5.3520			0.880	
			25.0-inf	31.93	1	0.4950			0.004	
FSI	LAP	4.8079	0.0-10.0	.	.	.			24	0.4173
			10.0-35.0	28.25	24	4.5509			22	2.6048
			35.0-inf	36.47	3	1.8930			2	1.2984
	PD	2.6445	0.0-10.0	5.58	3	1.3398				
			10.0-35.0	23.30	41	1.0473				
			35.0-inf	40.79	10	0.6738			Bias	
	FD	2.7860	0.0-10.0	6.55	2	0.9220			0.3131	
			10.0-35.0	23.59	20	1.3946				
			35.0-inf	40.97	5	1.1068			P (i)	
	S/H	8.0627	0.0-10.0	7.41	14	3.8103			0.028	
			10.0-35.0	24.29	546	7.6994			0.866	
			35.0-inf	38.31	58	8.4857			0.107	
CLAY	LAP	2.6935	0.0-5.0	3.51	15	0.4865	0	(0.0)	31	0.5966
			5.0-20.0	6.51	12	1.6060	1	(8.3)	10	2.0840
			20.0-inf	.	.	.	.	.	.	.
	PD	1.8156	0.0-5.0	3.88	2	0.4610	0	(0.0)		
			5.0-20.0	14.31	41	0.7006	1	(2.4)		
			20.0-inf	31.52	11	0.5568	0	(0.0)	Bias	
	FD	2.0510	0.0-5.0	4.20	1	0.2828	0	(0.0)	-0.6070	
			5.0-20.0	14.43	21	1.1761	0	(0.0)		
			20.0-inf	32.72	5	0.9930	0	(0.0)	P (i)	
	S/H	7.5782	0.0-5.0	2.55	1	0.6364			0.003	
			5.0-20.0	14.63	420	6.9824			0.680	
			20.0-inf	25.03	197	8.1818			0.317	
PH_H2O	LAP	0.0847	0.0-5.0	4.91	15	0.0381	0	(0.0)	13	0.0493
			5.0-inf	5.11	12	0.0662	3	(25.0)	37	0.1267
	PD	0.0933	0.0-5.0	4.56	45	0.0580	4	(8.9)		
			5.0-inf	5.41	9	0.0468	0	(0.0)	Bias	
	FD	0.1189	0.0-5.0	4.57	23	0.0823	0	(0.0)	-0.0319	
			5.0-inf	5.46	4	0.1433	1	(25.0)	P (i)	
	S/H	0.4741	0.0-5.0	4.59	499	0.4285			0.808	
			5.0-inf	5.26	119	0.6362			0.192	
PH_002M	LAP	0.0883	0.0-3.5	.	.	.	.	.	.	.
			3.5-4.5	4.43	10	0.0299	0	(0.0)	9	0.0678
			4.5-inf	4.70	17	0.0611	1	(5.9)	40	0.1152
	PD	0.0997	0.0-3.5	3.36	4	0.0429	0	(0.0)		
			3.5-4.5	4.18	45	0.0635	1	(2.2)		
			4.5-inf	5.02	5	0.0318	0	(0.0)	Bias	
	FD	0.1285	0.0-3.5	3.35	2	0.0960	0	(0.0)	0.0278	
			3.5-4.5	4.20	23	0.1042	2	(8.7)		
			4.5-inf	5.11	2	0.0738	0	(0.0)	P (i)	
	S/H	0.4404	0.0-3.5	3.30	12	0.1763			0.032	
			3.5-4.5	4.15	507	0.3808			0.806	
			4.5-inf	4.84	99	0.7434			0.162	

(continued)

Table C-1. Continued

Parameter	Data set[a]	Delta	Interval	Mean	Within-batch		Pairs>MQO		Between-batch	
					df	SD	n	(%)	df	SD
PH_01M	LAP	0.0588	0.0-4.4	4.28	12	0.0249	0	(0.0)	11	0.0460
			4.4-inf	4.56	15	0.0365	0	(0.0)	39	0.0591
	PD	0.0619	0.0-4.4	3.97	52	0.0351	0	(0.0)		
			4.4-inf	5.64	2	0.0050	0	(0.0)	Bias	
	FD	0.0818	0.0-4.4	3.97	26	0.0679	0	(0.0)	-0.0213	
			4.4-inf	5.65	1	0.0071	0	(0.0)	P (i)	
	S/H	0.4103	0.0-4.4	3.92	527	0.3491			0.860	
			4.4-inf	4.61	91	0.7618			0.140	
CA_CL	LAP	0.0299	0.0-0.2	.	.	.	.	.	26	0.0299
			0.2-1.0	0.31	27	0.0209	2	(7.4)	25	0.0211
			1.0-1.5	.	.	.	.	.	.	.
			1.5-inf	.	.	.	.	.	.	.
	PD	0.0642	0.0-0.2	0.06	32	0.0074	0	(0.0)		
			0.2-1.0	0.46	15	0.0253	1	(6.7)		
			1.0-1.5	.	.	.	.	.		
			1.5-inf	3.46	7	0.1629	0	(0.0)	Bias	
	FD	0.1567	0.0-0.2	0.07	17	0.0430	2	(11.8)	-0.0026	
			0.2-1.0	0.50	6	0.0642	0	(0.0)		
			1.0-1.5	1.17	1	1.1194	1	(100.0)		
			1.5-inf	3.70	3	0.1343	0	(0.0)	P (i)	
	S/H	1.1138	0.0-0.2	0.10	108	0.1487			0.194	
			0.2-1.0	0.45	328	0.8439			0.507	
			1.0-1.5	1.24	43	1.2642			0.073	
			1.5-inf	2.41	139	2.5039			0.225	
MG_CL	LAP	0.0145	0.0-0.2	0.07	27	0.0116	1	(3.7)	51	0.0087
			0.2-1.5	.	.	.	.	.	.	.
			1.5-inf	.	.	.	.	.	.	.
	PD	0.0144	0.0-0.2	0.05	46	0.0128	2	(4.3)		
			0.2-1.5	0.43	4	0.0111	0	(0.0)		
			1.5-inf	1.71	4	0.0772	0	(0.0)	Bias	
	FD	0.0308	0.0-0.2	0.05	23	0.0136	0	(0.0)	0.0011	
			0.2-1.5	0.44	2	0.0445	0	(0.0)		
			1.5-inf	1.74	2	0.0581	0	(0.0)	P (i)	
	S/H	0.4737	0.0-0.2	0.11	302	0.2219			0.493	
			0.2-1.5	0.56	310	0.6548			0.490	
			1.5-inf	2.35	6	2.5086			0.017	
K_CL	LAP	0.0065	0.0-0.04	.	.	.	.	.	26	0.0037
			0.04-0.07	0.06	14	0.0043	0	(0.0)	13	0.0045
			0.07-0.2	0.09	13	0.0037	0	(0.0)	12	0.0054
			0.2-inf	.	.	.	.	.	.	.
	PD	0.0080	0.0-0.04	0.03	11	0.0027	0	(0.0)		
			0.04-0.07	0.06	23	0.0045	0	(0.0)		
			0.07-0.2	0.13	20	0.0065	0	(0.0)		
			0.2-inf	.	.	.	.	.	Bias	
	FD	0.0074	0.0-0.04	0.03	6	0.0044	0	(0.0)	0.0009	
			0.04-0.07	0.06	11	0.0066	0	(0.0)		
			0.07-0.2	0.13	10	0.0048	0	(0.0)		
			0.2-inf	.	.	.	.	.	P (i)	
	S/H	0.1003	0.0-0.04	0.03	5	0.0102			0.015	
			0.04-0.07	0.06	98	0.0304			0.162	
			0.07-0.2	0.11	439	0.0721			0.688	
			0.2-inf	0.29	76	0.3378			0.134	

(continued)

Table C-1. Continued

Parameter	Data set[a]	Delta	Interval	Mean	Within-batch df	Within-batch SD	Pairs>MQO n	Pairs>MQO (%)	Between-batch df	Between-batch SD
NA_CL	LAP	0.0043	0.0-0.01	.	.	.	.	.	20	0.0027
			0.01-0.04	0.03	15	0.0048	0	(0.0)	14	0.0044
			0.04-0.2	0.07	12	0.0065	0	(0.0)	11	0.0060
			0.2-inf	.	.	.	.	.	.	.
	PD	0.0056	0.0-0.01	0.01	42	0.0027	0	(0.0)		
			0.01-0.04	0.02	6	0.0071	0	(0.0)		
			0.04-0.2	0.06	2	0.0000	0	(0.0)		
			0.2-inf	.	.	.	.	.	Bias	
	FD	0.0061	0.0-0.01	0.01	19	0.0034	0	(0.0)	-0.0014	
			0.01-0.04	0.02	5	0.0077	0	(0.0)		
			0.04-0.2	0.06	1	0.0007	0	(0.0)		
			0.2-inf	.	.	.	.	.	P (i)	
	S/H	0.0123	0.0-0.01	0.01	397	0.0074			0.642	
			0.01-0.04	0.02	217	0.0195			0.350	
			0.04-0.2	0.05	4	0.0239			0.008	
			0.2-inf	.	.	.			.	
AL_CL	LAP	0.4125	0.0-1.3	.	.	.	.	.	26	0.0866
			1.3-3.0	1.83	15	0.4926	1	(6.7)	13	0.1641
			3.0-6.0	3.59	12	0.2775	1	(8.3)	11	0.2159
			6.0-inf	.	.	.	.	.	.	.
	PD	0.3079	0.0-1.3	0.42	3	0.0345	0	(0.0)		
			1.3-3.0	2.35	18	0.1757	0	(0.0)		
			3.0-6.0	3.88	25	0.2581	0	(0.0)		
			6.0-inf	7.86	8	0.3119	0	(0.0)	Bias	
	FD	0.3214	0.0-1.3	0.03	1	0.0233	0	(0.0)	-0.0615	
			1.3-3.0	2.26	9	0.2575	0	(0.0)		
			3.0-6.0	3.86	13	0.2714	0	(0.0)		
			6.0-inf	7.75	4	0.2503	0	(0.0)	P (i)	
	S/H	2.5307	0.0-1.3	0.66	3	0.6176			0.011	
			1.3-3.0	2.06	181	1.7403			0.293	
			3.0-6.0	4.52	340	2.6185			0.523	
			6.0-inf	7.93	94	3.6846			0.172	
CA_OAC	LAP	0.0317	0.0-0.2	.	.	.	.	.	26	0.0277
			0.2-1.0	0.27	27	0.0242	4	(14.8)	25	0.0229
			1.0-5.0	.	.	.	.	.	.	.
			5.0-inf	.	.	.	.	.	.	.
	PD	0.0551	0.0-0.2	0.06	33	0.0070	2	(6.1)		
			0.2-1.0	0.46	14	0.0296	2	(14.3)		
			1.0-5.0	2.26	5	0.0923	0	(0.0)		
			5.0-inf	6.52	2	0.4203	0	(0.0)	Bias	
	FD	0.2962	0.0-0.2	0.07	18	0.0394	3	(16.7)	0.0004	
			0.2-1.0	0.53	5	0.0699	1	(20.0)		
			1.0-5.0	1.93	3	0.8623	1	(33.3)		
			5.0-inf	6.32	1	0.6548	0	(0.0)	P (i)	
	S/H	1.0906	0.0-0.2	0.10	113	0.1457			0.204	
			0.2-1.0	0.46	326	0.8691			0.505	
			1.0-5.0	1.89	173	1.9978			0.281	
			5.0-inf	6.64	6	5.6608			0.011	
MG_OAC	LAP	0.0168	0.0-0.2	0.07	27	0.0142	3	(11.1)	51	0.0090
			0.2-0.5	.	.	.	.	.	.	.
			0.5-inf	.	.	.	.	.	.	.
	PD	0.0189	0.0-0.2	0.05	46	0.0095	3	(6.5)		
			0.2-0.5	0.37	3	0.0063	0	(0.0)		
			0.5-inf	1.42	5	0.0433	0	(0.0)	Bias	
	FD	0.0258	0.0-0.2	0.05	23	0.0143	0	(0.0)	0.0006	
			0.2-0.5	0.33	1	0.0035	0	(0.0)		
			0.5-inf	1.24	3	0.0661	0	(0.0)	P (i)	
	S/H	0.4462	0.0-0.2	0.11	301	0.2162			0.493	
			0.2-0.5	0.34	158	0.4314			0.257	
			0.5-inf	0.90	159	0.9137			0.250	

(continued)

Table C-1. Continued

Parameter	Data set*	Delta	Interval	Mean	Within-batch df	Within-batch SD	Pairs>MQO n	Pairs>MQO (%)	Between-batch df	Between-batch SD
K_OAC	LAP	0.0092	0.0-0.05	.	.	.	.	.	26	0.0045
			0.05-0.1	0.08	27	0.0053	0	(0.0)	25	0.0049
			0.1-0.2	.	.	.	.	.	.	.
			0.2-inf	.	.	.	.	.	.	.
	PD	0.0127	0.0-0.05	0.04	16	0.0040	0	(0.0)		
			0.05-0.1	0.07	28	0.0033	0	(0.0)		
			0.1-0.2	0.16	7	0.0199	2	(28.6)		
			0.2-inf	0.22	3	0.0153	0	(0.0)	Bias	
	FD	0.0109	0.0-0.05	0.04	7	0.0058	0	(0.0)	0.0059	
			0.05-0.1	0.07	15	0.0073	0	(0.0)		
			0.1-0.2	0.15	3	0.0052	0	(0.0)		
			0.2-inf	0.21	2	0.0172	0	(0.0)	P (i)	
	S/H	0.0948	0.0-0.05	0.04	21	0.0197			0.043	
			0.05-0.1	0.08	364	0.0378			0.563	
			0.1-0.2	0.15	160	0.1033			0.262	
			0.2-inf	0.31	73	0.3414			0.132	
NA_OAC	LAP	0.0062	0.0-0.02	.	.	.	.	.	26	0.0028
			0.02-0.2	0.05	27	0.0050	0	(0.0)	25	0.0048
			0.2-inf	.	.	.	.	.	.	.
	PD	0.0067	0.0-0.02	0.01	49	0.0026	0	(0.0)		
			0.02-0.2	0.04	5	0.0051	0	(0.0)		
			0.2-inf	.	.	.	.	.	Bias	
	FD	0.0075	0.0-0.02	0.01	25	0.0037	0	(0.0)	0.0043	
			0.02-0.2	0.04	2	0.0070	0	(0.0)		
			0.2-inf	.	.	.	.	.	P (i)	
	S/H	0.0144	0.0-0.02	0.01	482	0.0080			0.640	
			0.02-0.2	0.03	136	0.0219			0.180	
			0.2-inf	.	.	.			.	
CEC_CL	LAP	0.5139	0.0-2.5	.	.	.	.	.	26	0.1239
			2.5-5.5	4.41	14	0.1794	0	(0.0)	13	0.2513
			5.5-12.0	7.38	13	0.4005	1	(7.7)	12	0.4411
			12.0-inf	.	.	.	.	.	.	.
	PD	0.5345	0.0-2.5	2.28	3	0.1389	0	(0.0)		
			2.5-5.5	4.41	28	0.2426	1	(3.6)		
			5.5-12.0	7.79	19	0.2258	0	(0.0)		
			12.0-inf	15.12	4	1.9403	1	(25.0)	Bias	
	FD	0.5532	0.0-2.5	2.31	1	0.1648	0	(0.0)	-0.0123	
			2.5-5.5	4.29	14	0.2213	0	(0.0)		
			5.5-12.0	7.62	10	0.4741	0	(0.0)		
			12.0-inf	16.08	2	0.4530	0	(0.0)	P (i)	
	S/H	2.8580	0.0-2.5	2.43	4	0.2681			0.008	
			2.5-5.5	4.68	161	2.0715			0.257	
			5.5-12.0	7.81	429	2.9760			0.680	
			12.0-inf	14.65	24	4.9874			0.055	
CEC_OAC	LAP	1.4645	0.0-2.5	.	.	.	.	.	26	0.1656
			2.5-18.0	10.99	14	0.4452	0	(0.0)	13	1.2431
			18.0-inf	22.66	13	1.4873	2	(15.4)	12	1.8608
	PD	1.7128	0.0-2.5	.	.	.	.	.		
			2.5-18.0	8.31	52	0.7602	4	(7.7)		
			18.0-inf	28.13	2	3.5041	1	(50.0)	Bias	
	FD	1.6816	0.0-2.5	.	.	.	.	.	-0.4022	
			2.5-18.0	8.26	26	1.0254	1	(3.8)		
			18.0-inf	26.40	1	0.2185	0	(0.0)	P (i)	
	S/H	4.6847	0.0-2.5	.	.	.			.	
			2.5-18.0	9.38	582	4.1804			0.919	
			18.0-inf	23.82	36	7.9077			0.081	

(continued)

Table C-1. Continued

Parameter	Data set[a]	Delta	Interval	Mean	Within-batch df	Within-batch SD	Pairs>MQO n	Pairs>MQO (%)	Between-batch df	Between-batch SD
AC_BACL	LAP	1.6683	0.0-6.7	.	.	.	.	.	24	0.4623
			6.7-20.0	16.30	14	1.0665	1	(7.1)	13	1.4877
			20.0-inf	29.02	13	1.6857	0	(0.0)	12	2.5234
	PD	1.6590	0.0-6.7	5.37	19	0.6044	1	(5.3)		
			6.7-20.0	10.50	32	0.5668	0	(0.0)		
			20.0-inf	26.50	3	3.1085	0	(0.0)	Bias	
	FD	1.8373	0.0-6.7	5.51	11	0.9879	0	(0.0)	-0.1415	
			6.7-20.0	11.28	15	0.9447	0	(0.0)		
			20.0-inf	32.13	1	3.0059	0	(0.0)	P (i)	
	S/H	5.5839	0.0-6.7	5.71	131	3.3224			0.210	
			6.7-20.0	10.84	444	5.7101			0.692	
			20.0-inf	25.80	43	7.7319			0.097	
CA_CL2	LAP	0.0490	0.0-0.4	.	.	.	.	.	.	.
			0.4-1.0	0.57	27	0.0181	0	(0.0)	51	0.0382
			1.0-inf	.	.	.	.	.	.	.
	PD	0.0473	0.0-0.4	0.38	2	0.0356	1	(50.0)		
			0.4-1.0	0.58	52	0.0132	0	(0.0)		
			1.0-inf	.	.	.	.	.	Bias	
	FD	0.0476	0.0-0.4	0.36	1	0.0021	0	(0.0)	0.0249	
			0.4-1.0	0.58	26	0.0157	0	(0.0)		
			1.0-inf	.	.	.	.	.	P (i)	
	S/H	0.1056	0.0-0.4	0.36	8	0.1353			0.027	
			0.4-1.0	0.53	610	0.0943			0.973	
			1.0-inf	.	.	.			.	
MG_CL2	LAP	0.0075	0.0-0.05	0.04	15	0.0058	1	(6.7)	39	0.0057
			0.05-0.08	0.06	12	0.0023	0	(0.0)	11	0.0048
			0.08-0.2	.	.	.	.	.	.	.
			0.2-inf	.	.	.	.	.	.	.
	PD	0.0053	0.0-0.05	0.02	37	0.0020	1	(2.7)		
			0.05-0.08	0.07	9	0.0060	1	(11.1)		
			0.08-0.2	0.15	6	0.0014	0	(0.0)		
			0.2-inf	0.29	2	0.0099	0	(0.0)	Bias	
	FD	0.0087	0.0-0.05	0.02	19	0.0048	1	(5.3)	0.0024	
			0.05-0.08	0.07	4	0.0089	0	(0.0)		
			0.08-0.2	0.15	3	0.0074	0	(0.0)		
			0.2-inf	0.30	1	0.0184	0	(0.0)	P (i)	
	S/H	0.0841	0.0-0.05	0.04	209	0.0635			0.330	
			0.05-0.08	0.07	105	0.0743			0.178	
			0.08-0.2	0.13	277	0.0951			0.445	
			0.2-inf	0.28	27	0.1597			0.047	
K_CL2	LAP	0.0027	0.0-0.02	0.02	24	0.0013	0	(0.0)	48	0.0025
			0.02-0.05	0.03	3	0.0009	0	(0.0)	2	0.0020
			0.05-inf	.	.	.	.	.	.	.
	PD	0.0029	0.0-0.02	0.01	44	0.0009	0	(0.0)		
			0.02-0.05	0.04	9	0.0029	2	(22.2)		
			0.05-inf	0.05	1	0.0021	0	(0.0)	Bias	
	FD	0.0039	0.0-0.02	0.01	22	0.0013	0	(0.0)	0.0005	
			0.02-0.05	0.04	5	0.0060	0	(0.0)		
			0.05-inf	.	.	.	.	.	P (i)	
	S/H	0.0220	0.0-0.02	0.02	430	0.0095			0.668	
			0.02-0.05	0.04	157	0.0348			0.272	
			0.05-inf	0.08	31	0.1006			0.060	

(continued)

Table C-1. Continued

Parameter	Data set*	Delta	Interval	Mean	Within-batch		Pairs>MQO		Between-batch	
					df	SD	n	(%)	df	SD
NA_CL2	LAP	0.0046	0.0-0.01	0.01	2	0.0046	0	(0.0)	27	0.0015
			0.01-0.03	0.02	12	0.0010	0	(0.0)	11	0.0020
			0.03-0.05	0.05	11	0.0067	2	(18.2)	10	0.0054
			0.05-inf	0.06	2	0.0021	0	(0.0)	1	0.0060
	PD	0.0023	0.0-0.01	0.01	50	0.0009	0	(0.0)		
			0.01-0.03	0.03	4	0.0012	0	(0.0)		
			0.03-0.05	.	.	.	.	.		
			0.05-inf	.	.	.	.	.	Bias	
	FD	0.0024	0.0-0.01	0.01	25	0.0011	0	(0.0)	0.0013	
			0.01-0.03	0.03	2	0.0016	0	(0.0)		
			0.03-0.05	.	.	.	.	.		
			0.05-inf	.	.	.	.	.	P (i)	
	S/H	0.0092	0.0-0.01	0.01	505	0.0074			0.819	
			0.01-0.03	0.02	111	0.0166			0.176	
			0.03-0.05	0.04	2	0.0065			0.005	
			0.05-inf	.	.	.			.	
FE_CL2	LAP	0.0012	0.0-0.00	0.00	8	0.0007	0	(0.0)	29	0.0006
			0.00-0.02	0.01	9	0.0007	0	(0.0)	8	0.0013
			0.02-0.07	.	.	.	.	.	.	.
			0.07-inf	.	.	.	.	.	.	.
	PD	0.0019	0.0-0.00	0.00	22	0.0012	0	(0.0)		
			0.00-0.02	0.00	1	0.0035	0	(0.0)		
			0.02-0.07	0.03	2	0.0020	0	(0.0)		
			0.07-inf	.	.	.	.	.	Bias	
	FD	0.0014	0.0-0.00	0.00	12	0.0010	0	(0.0)	-0.0004	
			0.00-0.02	0.00	1	0.0014	0	(0.0)		
			0.02-0.07	0.03	1	0.0028	0	(0.0)		
			0.07-inf	.	.	.	.	.	P (i)	
	S/H	0.0195	0.0-0.00	0.00	469	0.0027			0.715	
			0.00-0.02	0.01	103	0.0163			0.184	
			0.02-0.07	0.03	11	0.0477			0.025	
			0.07-inf	0.16	22	0.3604			0.035	
AL_CL2	LAP	0.0092	0.0-0.03	0.01	14	0.0039	0	(0.0)	35	0.0044
			0.03-0.07	0.05	12	0.0049	0	(0.0)	11	0.0083
			0.07-0.1	0.09	1	0.0092	0	(0.0)	0	.
			0.1-0.3	.	.	.	.	.	.	.
			0.3-inf	.	.	.	.	.	.	.
	PD	0.0066	0.0-0.03	0.02	7	0.0021	0	(0.0)		
			0.03-0.07	0.04	10	0.0026	0	(0.0)		
			0.07-0.1	0.12	29	0.0059	0	(0.0)		
			0.1-0.3	0.21	6	0.0025	0	(0.0)		
			0.3-inf	.	.	.	.	.	Bias	
	FD	0.0092	0.0-0.03	0.02	3	0.0035	0	(0.0)	0.0023	
			0.03-0.07	0.04	6	0.0151	0	(0.0)		
			0.07-0.1	0.12	14	0.0072	0	(0.0)		
			0.1-0.3	0.21	3	0.0054	0	(0.0)		
			0.3-inf	.	.	.	.	.	P (i)	
	S/H	0.0946	0.0-0.03	0.02	59	0.0365			0.104	
			0.03-0.07	0.05	114	0.0579			0.186	
			0.07-0.1	0.12	419	0.0965			0.652	
			0.1-0.3	0.21	26	0.3005			0.056	
			0.3-inf	.	.	.			.	

(continued)

Table C-1. Continued

Parameter	Data set*	Delta	Interval	Mean	Within-batch df	Within-batch SD	Pairs>MQO n	Pairs>MQO (%)	Between-batch df	Between-batch SD
FE_PYP	LAP	0.0321	0.0-0.3	.	.	.	.	.	25	0.0082
			0.3-0.7	0.62	12	0.0202	0	(0.0)	11	0.0313
			0.7-inf	0.76	15	0.0266	0	(0.0)	13	0.0532
	PD	0.0357	0.0-0.3	0.18	32	0.0133	1	(3.1)		
			0.3-0.7	0.45	20	0.0269	0	(0.0)		
			0.7-inf	1.07	2	0.0244	0	(0.0)	Bias	
	FD	0.0395	0.0-0.3	0.18	16	0.0213	0	(0.0)	-0.0176	
			0.3-0.7	0.45	10	0.0286	0	(0.0)		
			0.7-inf	1.05	1	0.0474	0	(0.0)	P (i)	
	S/H	0.3058	0.0-0.3	0.19	294	0.1869			0.478	
			0.3-0.7	0.45	296	0.3774			0.459	
			0.7-inf	0.95	28	0.6662			0.063	
AL_PYP	LAP	0.0252	0.0-0.1	.	.	.	.	.	26	0.0140
			0.1-0.3	.	.	.	.	.	.	.
			0.3-0.7	0.54	14	0.0412	1	(7.1)	13	0.0379
			0.7-inf	0.84	13	0.0331	0	(0.0)	12	0.0665
	PD	0.0222	0.0-0.1	0.10	26	0.0116	1	(3.8)		
			0.1-0.3	0.22	19	0.0188	2	(10.5)		
			0.3-0.7	0.36	9	0.0181	0	(0.0)		
			0.7-inf	.	.	.	.	.	Bias	
	FD	0.0274	0.0-0.1	0.10	13	0.0134	0	(0.0)	-0.0037	
			0.1-0.3	0.21	9	0.0267	0	(0.0)		
			0.3-0.7	0.36	5	0.0335	0	(0.0)		
			0.7-inf	.	.	.	.	.	P (i)	
	S/H	0.1647	0.0-0.1	0.10	250	0.0578			0.413	
			0.1-0.3	0.21	289	0.1812			0.445	
			0.3-0.7	0.37	79	0.4194			0.141	
			0.7-inf	1.02	0	.			0.001	
FE_AO	LAP	0.0469	0.0-0.2	.	.	.	.	.	25	0.0249
			0.2-0.3	.	.	.	.	.	.	.
			0.3-0.6	.	.	.	.	.	.	.
			0.6-inf	0.99	27	0.0413	0	(0.0)	25	0.0806
	PD	0.0343	0.0-0.2	0.12	25	0.0412	1	(4.0)		
			0.2-0.3	0.23	10	0.0177	1	(10.0)		
			0.3-0.6	0.41	15	0.0246	0	(0.0)		
			0.6-inf	0.72	4	0.0371	0	(0.0)	Bias	
	FD	0.0448	0.0-0.2	0.13	14	0.0613	1	(7.1)	0.0107	
			0.2-0.3	0.24	4	0.0250	0	(0.0)		
			0.3-0.6	0.42	7	0.0377	0	(0.0)		
			0.6-inf	0.71	2	0.0305	0	(0.0)	P (i)	
	S/H	0.2684	0.0-0.2	0.15	102	0.1043			0.182	
			0.2-0.3	0.26	184	0.2411			0.281	
			0.3-0.6	0.41	292	0.3192			0.455	
			0.6-inf	0.79	40	0.4292			0.081	
AL_AO	LAP	0.0224	0.0-0.3	.	.	.	.	.	26	0.0175
			0.3-1.1	0.87	14	0.0345	0	(0.0)	13	0.0430
			1.1-inf	1.41	13	0.0718	1	(7.7)	12	0.0555
	PD	0.0286	0.0-0.3	0.15	41	0.0189	1	(2.4)		
			0.3-1.1	0.37	13	0.0208	1	(7.7)		
			1.1-inf	.	.	.	.	.	Bias	
	FD	0.0360	0.0-0.3	0.14	20	0.0273	1	(5.0)	0.0018	
			0.3-1.1	0.36	7	0.0423	0	(0.0)		
			1.1-inf	.	.	.	.	.	P (i)	
	S/H	0.1311	0.0-0.3	0.17	551	0.1152			0.874	
			0.3-1.1	0.37	67	0.2277			0.126	
			1.1-inf	.	.	.			.	

(continued)

Table C-1. Continued

Parameter	Data set*	Delta	Interval	Mean	Within-batch		Pairs>MQO		Between-batch	
					df	SD	n	(%)	df	SD
SI_AO	LAP	0.0106	0.0-0.05	.	.	.	.	.	25	0.0094
			0.05-0.3	0.22	18	0.0154	1	(5.6)	16	0.0368
			0.3-inf	0.35	9	0.0422	3	(33.3)	7	0.0572
	PD	0.0138	0.0-0.05	0.02	38	0.0087	0	(0.0)		
			0.05-0.3	0.08	8	0.0186	1	(12.5)		
			0.3-inf	.	.	.	.	.	Bias	
	FD	0.0137	0.0-0.05	0.02	19	0.0085	0	(0.0)	-0.0034	
			0.05-0.3	0.08	4	0.0168	0	(0.0)		
			0.3-inf	.	.	.	.	.	P (i)	
	S/H	0.0292	0.0-0.05	0.02	606	0.0256			0.969	
			0.05-0.3	0.08	8	0.1124			0.019	
			0.3-inf	.	.	.			.	
FE_CD	LAP	0.1088	0.0-0.3	.	.	.	.	.	26	0.0312
			0.3-2.5	1.59	27	0.0495	0	(0.0)	25	0.0971
			2.5-3.0	.	.	.	.	.	.	.
			3.0-inf	.	.	.	.	.	.	.
	PD	0.2893	0.0-0.3	.	.	.	.	.		
			0.3-2.5	1.46	42	0.3193	3	(7.1)		
			2.5-3.0	2.77	5	0.0677	0	(0.0)		
			3.0-inf	3.71	7	0.1193	0	(0.0)	Bias	
	FD	0.1367	0.0-0.3	.	.	.	.	.	0.0123	
			0.3-2.5	1.46	21	0.0935	0	(0.0)		
			2.5-3.0	2.81	2	0.0863	0	(0.0)		
			3.0-inf	3.72	4	0.2223	0	(0.0)	P (i)	
	S/H	0.8260	0.0-0.3	0.22	4	0.1347			0.009	
			0.3-2.5	1.67	505	0.7575			0.818	
			2.5-3.0	2.63	59	0.9675			0.095	
			3.0-inf	3.29	50	1.3848			0.079	
AL_CD	LAP	0.0248	0.0-0.2	.	.	.	.	.	26	0.0099
			0.2-0.3	.	.	.	.	.	.	.
			0.3-0.8	0.63	14	0.0265	0	(0.0)	13	0.0375
			0.8-inf	1.12	13	0.0792	2	(15.4)	12	0.1044
	PD	0.0259	0.0-0.2	0.17	23	0.0045	0	(0.0)		
			0.2-0.3	0.26	14	0.0340	1	(7.1)		
			0.3-0.8	0.40	17	0.0136	0	(0.0)		
			0.8-inf	.	.	.	.	.	Bias	
	FD	0.0250	0.0-0.2	0.17	11	0.0096	0	(0.0)	0.0032	
			0.2-0.3	0.26	7	0.0254	0	(0.0)		
			0.3-0.8	0.39	9	0.0146	0	(0.0)		
			0.8-inf	.	.	.	.	.	P (i)	
	S/H	0.1247	0.0-0.2	0.17	261	0.0980			0.434	
			0.2-0.3	0.27	176	0.1192			0.269	
			0.3-0.8	0.35	181	0.1635			0.297	
			0.8-inf	.	.	.			.	
SO4_H2O	LAP	1.6327	0.0-7.0	.	.	.	.	.	25	0.6444
			7.0-15.0	12.77	11	1.6719	1	(9.1)	10	1.4299
			15.0-18.0	15.90	3	0.6183	0	(0.0)	1	0.0361
			18.0-inf	20.79	13	1.5771	2	(15.4)	12	1.1352
	PD	1.6279	0.0-7.0	3.74	4	0.4821	0	(0.0)		
			7.0-15.0	11.85	30	1.3852	2	(6.7)		
			15.0-18.0	15.83	10	1.5625	1	(10.0)		
			18.0-inf	23.28	10	0.7616	0	(0.0)	Bias	
	FD	1.9181	0.0-7.0	3.54	2	0.5884	0	(0.0)	0.1264	
			7.0-15.0	12.11	17	1.7065	1	(5.9)		
			15.0-18.0	16.47	3	2.5084	0	(0.0)		
			18.0-inf	23.05	5	0.6322	0	(0.0)	P (i)	
	S/H	27.1745	0.0-7.0	4.79	74	3.3512			0.145	
			7.0-15.0	11.19	296	5.4730			0.481	
			15.0-18.0	15.94	128	6.1761			0.190	
			18.0-inf	46.59	120	123.979			0.184	

(continued)

Table C-1. Continued

Parameter	Data set*	Delta	Interval	Mean	Within-batch df	Within-batch SD	Pairs>MQO n	Pairs>MQO (%)	Between-batch df	Between-batch SD
SO4_PO4	LAP	12.1608	0.0-15.0	.	.	.	.	.	26	1.7715
			15.0-50.0	.	.	.	.	.	.	.
			50.0-100.0	79.25	15	11.0785	1	(6.7)	13	9.6793
			100.0-inf	111.9	12	3.5698	0	(0.0)	11	7.0690
	PD	6.8784	0.0-15.0	4.11	2	1.4634	1	(50.0)		
			15.0-50.0	30.82	29	3.8895	2	(6.9)		
			50.0-100.0	68.92	19	2.8575	0	(0.0)		
			100.0-inf	121.6	4	0.9397	0	(0.0)		Bias
	FD	7.9622	0.0-15.0	4.62	1	2.5597	0	(0.0)		2.0085
			15.0-50.0	29.95	14	5.5835	2	(14.3)		
			50.0-100.0	68.80	10	4.7724	0	(0.0)		
			100.0-inf	121.8	2	5.0722	0	(0.0)		P (i)
	S/H	49.5081	0.0-15.0	8.81	49	4.6368				0.108
			15.0-50.0	29.07	256	28.2552				0.429
			50.0-100.0	69.10	292	54.1880				0.430
			100.0-inf	260.2	21	393.295				0.033
SO4_0	LAP	0.1111	0.0-1.0	.	.	.	.	.	26	0.1200
			1.0-2.0	1.33	14	0.0539	0	(0.0)	12	0.0826
			2.0-inf	2.12	13	0.1082	6	(46.2)	12	0.0498
	PD	0.1029	0.0-1.0	0.75	10	0.0344	0	(0.0)		
			1.0-2.0	1.38	31	0.0449	0	(0.0)		
			2.0-inf	2.44	13	0.0423	0	(0.0)		Bias
	FD	0.1417	0.0-1.0	0.74	5	0.0179	0	(0.0)		0.0365
			1.0-2.0	1.41	16	0.1254	2	(12.5)		
			2.0-inf	2.47	6	0.0652	0	(0.0)		P (i)
	S/H	3.3925	0.0-1.0	0.69	97	0.4000				0.178
			1.0-2.0	1.44	449	0.6145				0.700
			2.0-inf	8.27	72	23.7904				0.121
SO4_2	LAP	0.1262	0.0-2.0	1.95	1	0.0608	0	(0.0)	.	.
			2.0-2.7	2.16	12	0.0437	0	(0.0)	37	0.1347
			2.7-inf	3.13	14	0.0603	0	(0.0)	13	0.0858
	PD	0.1337	0.0-2.0	1.79	12	0.0404	0	(0.0)		
			2.0-2.7	2.29	19	0.0704	0	(0.0)		
			2.7-inf	3.38	23	0.0813	0	(0.0)		Bias
	FD	0.1496	0.0-2.0	1.81	7	0.0734	0	(0.0)		0.0445
			2.0-2.7	2.35	9	0.0991	0	(0.0)		
			2.7-inf	3.43	11	0.1020	0	(0.0)		P (i)
	S/H	5.3257	0.0-2.0	1.61	78	0.7585				0.133
			2.0-2.7	2.43	329	0.6049				0.505
			2.7-inf	5.20	211	13.5590				0.362
SO4_4	LAP	0.1726	0.0-2.0	.	.	.	.	.	.	.
			2.0-3.0	2.96	2	0.1228	1	(50.0)	1	0.0544
			3.0-3.7	3.23	11	0.0895	2	(18.2)	10	0.0926
			3.7-inf	4.19	14	0.1161	0	(0.0)	39	0.1591
	PD	0.1625	0.0-2.0	.	.	.	.	.		
			2.0-3.0	2.58	14	0.1073	1	(7.1)		
			3.0-3.7	3.40	13	0.0741	0	(0.0)		
			3.7-inf	4.68	27	0.0978	0	(0.0)		Bias
	FD	0.2191	0.0-2.0	.	.	.	.	.		0.0504
			2.0-3.0	2.58	7	0.1624	0	(0.0)		
			3.0-3.7	3.43	7	0.2384	0	(0.0)		
			3.7-inf	4.71	13	0.1120	0	(0.0)		P (i)
	S/H	6.3261	0.0-2.0	1.65	13	0.9980				0.023
			2.0-3.0	2.70	76	1.0777				0.126
			3.0-3.7	3.47	233	0.7779				0.345
			3.7-inf	5.93	296	11.6513				0.506

(continued)

Table C-1. Continued

Parameter	Data set*	Delta	Interval	Mean	Within-batch		Pairs>MQO		Between-batch	
					df	SD	n	(%)	df	SD
SO4_8	LAP	0.2954	0.0-2.0	.	.	.	.	.	.	.
			2.0-5.8	5.23	13	0.1490	1	(7.7)	12	0.3588
			5.8-7.5	6.45	14	0.1227	0	(0.0)	13	0.2314
			7.5-inf	.	.	.	.	.	26	0.2160
	PD	0.2966	0.0-2.0	.	.	.	.	.		
			2.0-5.8	4.82	21	0.1159	0	(0.0)		
			5.8-7.5	6.64	18	0.0883	0	(0.0)		
			7.5-inf	8.30	15	0.1707	0	(0.0)	Bias	
	FD	0.3807	0.0-2.0	.	.	.	.	.	0.0520	
			2.0-5.8	4.76	10	0.1999	0	(0.0)		
			5.8-7.5	6.55	9	0.2974	0	(0.0)		
			7.5-inf	8.25	8	0.2466	0	(0.0)	P (i)	
	S/H	5.2892	0.0-2.0	1.55	1	0.6322			0.003	
			2.0-5.8	5.13	192	1.5537			0.298	
			5.8-7.5	6.58	323	1.4406			0.499	
			7.5-inf	12.31	102	20.4390			0.200	
SO4_16	LAP	0.6141	0.0-2.0	.	.	.	.	.	.	.
			2.0-7.5	.	.	.	.	.	.	.
			7.5-12.0	10.95	18	0.2068	0	(0.0)	16	0.7376
			12.0-14.0	12.25	9	0.4184	1	(11.1)	8	0.3194
			14.0-inf	.	.	.	.	.	26	0.4227
	PD	0.5706	0.0-2.0	.	.	.	.	.		
			2.0-7.5	6.89	2	0.5507	1	(50.0)		
			7.5-12.0	10.03	18	0.1356	0	(0.0)		
			12.0-14.0	12.95	20	0.2247	0	(0.0)		
			14.0-inf	15.29	14	0.2112	0	(0.0)	Bias	
	FD	0.6337	0.0-2.0	.	.	.	.	.	0.1074	
			2.0-7.5	7.09	1	0.1478	0	(0.0)		
			7.5-12.0	10.04	9	0.2643	0	(0.0)		
			12.0-14.0	13.03	11	0.3853	0	(0.0)		
			14.0-inf	15.41	6	0.3208	0	(0.0)	P (i)	
	S/H	6.2114	0.0-2.0	.	.	.			.	
			2.0-7.5	5.13	1	1.3810			0.004	
			7.5-12.0	10.78	270	2.6221			0.418	
			12.0-14.0	12.96	233	2.1651			0.358	
			14.0-inf	19.04	114	19.4814			0.220	
SO4_32	LAP	1.2826	0.0-2.0	.	.	.	.	.	.	.
			2.0-18.0	.	.	.	.	.	.	.
			18.0-20.0	19.70	2	2.7652	1	(50.0)	0	.
			20.0-30.0	23.63	25	0.4631	1	(4.0)	23	1.2642
			30.0-inf	.	.	.	.	.	26	0.8822
	PD	1.3867	0.0-2.0	.	.	.	.	.		
			2.0-18.0	17.47	5	3.2481	1	(20.0)		
			18.0-20.0	19.89	1	0.2475	0	(0.0)		
			20.0-30.0	25.79	42	0.7429	1	(2.4)		
			30.0-inf	31.65	6	0.2473	0	(0.0)	Bias	
	FD	1.3435	0.0-2.0	.	.	.	.	.	0.0986	
			2.0-18.0	17.45	3	4.3546	1	(33.3)		
			18.0-20.0	.	.	.	.	.		
			20.0-30.0	25.68	21	0.5748	0	(0.0)		
			30.0-inf	31.63	3	0.3889	0	(0.0)	P (i)	
	S/H	7.1054	0.0-2.0	.	.	.			.	
			2.0-18.0	15.75	1	3.2937			0.007	
			18.0-20.0	19.34	2	3.5718			0.005	
			20.0-30.0	25.11	528	3.9387			0.827	
			30.0-inf	35.60	87	22.5927			0.161	

(continued)

Table C-1. Continued

Parameter	Data set[a]	Delta	Interval	Mean	Within-batch		Pairs>MQO		Between-batch	
					df	SD	n	(%)	df	SD
C_TOT	LAP	0.0835	0.0-0.5	.	.	.	.	.	26	0.0157
			0.5-2.5	1.46	14	0.0338	0	(0.0)	13	0.0349
			2.5-6.0	4.62	13	0.2986	2	(15.4)	12	0.1975
			6.0-inf	.	.	.	.	.	.	.
	PD	0.0715	0.0-0.5	0.26	28	0.0119	0	(0.0)		
			0.5-2.5	0.83	22	0.0470	1	(4.5)		
			2.5-6.0	4.80	2	0.0462	0	(0.0)		
			6.0-inf	7.66	2	0.0809	0	(0.0)	Bias	
	FD	0.1910	0.0-0.5	0.25	13	0.0502	1	(7.7)	-0.0339	
			0.5-2.5	0.79	12	0.1269	1	(8.3)		
			2.5-6.0	4.83	1	0.4992	0	(0.0)		
			6.0-inf	7.71	1	0.7481	0	(0.0)	P (i)	
	S/H	1.2144	0.0-0.5	0.31	279	0.3334			0.434	
			0.5-2.5	1.02	245	0.7593			0.387	
			2.5-6.0	3.58	50	2.0228			0.107	
			6.0-inf	7.55	44	7.7529			0.072	
N_TOT	LAP	0.0036	0.0-0.08	.	.	.	.	.	26	0.0006
			0.08-0.1	0.12	14	0.0053	1	(7.1)	13	0.0043
			0.1-0.3	0.22	13	0.0084	0	(0.0)	12	0.0070
			0.3-inf	.	.	.	.	.	.	.
	PD	0.0050	0.0-0.08	0.04	45	0.0040	0	(0.0)		
			0.08-0.1	0.10	5	0.0025	0	(0.0)		
			0.1-0.3	0.26	2	0.0036	0	(0.0)		
			0.3-inf	0.35	2	0.0056	0	(0.0)	Bias	
	FD	0.0084	0.0-0.08	0.04	23	0.0055	0	(0.0)	0.0017	
			0.08-0.1	0.10	2	0.0025	0	(0.0)		
			0.1-0.3	0.26	1	0.0163	0	(0.0)		
			0.3-inf	0.35	1	0.0290	0	(0.0)	P (i)	
	S/H	0.0534	0.0-0.08	0.04	465	0.0292			0.715	
			0.08-0.1	0.10	61	0.0599			0.109	
			0.1-0.3	0.20	65	0.1297			0.123	
			0.3-inf	0.40	27	0.1878			0.053	
S_TOT	LAP	0.0016	0.0-0.00	.	.	.	.	.	25	0.0004
			0.00-0.02	0.02	5	0.0011	0	(0.0)	4	0.0012
			0.02-0.04	0.03	22	0.0022	1	(4.5)	20	0.0016
			0.04-inf	.	.	.	.	.	.	.
	PD	0.0014	0.0-0.00	0.01	20	0.0007	1	(5.0)		
			0.00-0.02	0.01	26	0.0009	1	(3.8)		
			0.02-0.04	0.03	7	0.0007	0	(0.0)		
			0.04-inf	0.04	1	0.0001	0	(0.0)	Bias	
	FD	0.0018	0.0-0.00	0.01	11	0.0012	0	(0.0)	-0.0007	
			0.00-0.02	0.01	12	0.0011	0	(0.0)		
			0.02-0.04	0.03	4	0.0025	0	(0.0)		
			0.04-inf	.	.	.	.	.	P (i)	
	S/H	0.0267	0.0-0.00	0.01	172	0.0045			0.286	
			0.00-0.02	0.01	355	0.0080			0.542	
			0.02-0.04	0.03	48	0.0118			0.100	
			0.04-inf	0.14	43	0.2763			0.072	

[a] LAP = laboratory audit sample pairs; PD = preparation duplicates; FD = field duplicates; S/H = sampling class/horizon groups of routine samples.
inf = open-ended interval, i.e., infinity; df = degrees of freedom; SD = standard deviation; P(i) = proportion of routine samples in the ith interval.

Appendix D

Inordinate Data Points Influencing the Uncertainty Estimates

Appendix D provides information on specific data points that have an inordinate effect on the uncertainty estimates presented in the results and discussion for precision and accuracy in Section 3. Included is information on each parameter for each data set for the sampling class/horizon group, the batch/sample number, and the reason for its effect on the estimates. Data users interested in the quality of data in specific batches will find this table particularly helpful. The table is sorted by parameter and subsorted by data set.

Table D-1. Inordinate Data Points Having a High Degree of Influence on the Uncertainty Estimates for the Data Sets

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
MOIST	S/H	HST / Oe		large variability
	FD	HST / Oe	30131–14,19	high value
	PD	HST / Oe	30132–26,34	large variability
	AS	C	30127–10	high field audit value
		Bw	30127–4,23	large lab audit variability
SAND	FD	TXW / Bt	30113–25,6	large variability
	PD	TWD / C	30112–37,18	large variability
		TXW / Bt	30126–23,5	large variability
	AS	C	30118–6	low field audit value
		B	30106–3,34	high field audit value
VCOS	FD	BMK / B	30117–26,39	high value
		FLW / C	30120–34,32	high value
	PD	FLW / C	30120–34,38	large variability
		FLW / C	30120–32,20	high value
	AS	C	30120–23	high lab audit value
		B	30106–3,34	low field audit value
		Bw	30130–10,28	high lab audit value
COS	FD	TXW / Bt	30113–25,6	high value
		FLW / C	30120–34,32	large variability
		FLW / Cg	30121–1,19	large variability
	PD	FLW / C	30120–32,20	large variability
	AS	C	30120–23	high lab audit value
		B	30106–3,34	high field audit value
MS	S/H	BXW / E		large variability
		CFP / Ag		large variability
	FD	TXW / Bt	30113–25,6	large variability
		BMK / Bw	30117–26,39	large variability
		FLW / Cg	30121–1,19	large variability
	PD	FLW / C	30120–34,38	large variability
	AS	C	30118–6	low field audit value
		B	30114–16,36	high field audit value
FS	FD	CFP / C	30115–39,30	large variability
		BMK / Bw	30117–26,39	large variability
	PD	CFP / C	30115–39,6	large variability
	AS	C	30118–6	low field audit value
		B	30114–7,40	low field audit value
		B	30120–6,40	low field audit value
		Bw	30123–12,23	high field audit value
VFS	S/H	BNS / Cr		large variability
		BXW / E		large variability
	FD	BMK / Bw	30117–26,39	large variability
	PD	BMK / Bw	30117–39,23	large variability
	AS	Bw	30105–32,34	large field audit variability
		B	30108–9,27	low field audit value
		B	30120–6,40	large field audit variability
SILT	FD	TXW / Bt	30113–25,6	large variability
	PD	TXW / Bt	30126–23,5	large variability
	AS	C	30118–6	high field audit value
		C	30106–14	low field audit value
		B	30106–3,34	low field audit value
		Bw	30109–23,26	low lab audit value

(Continued)

Table D-1. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
COSI	FD	TXW / Bt	30113–25,6	large variability
		BMK / Bw	30117–26,39	low value
	PD	TXW / Bt	30126–23,5	high value
	AS	C	30118–6	high audit value
		B	30106–4,11	negative lab audit value
		Bw	30115–10,28	high field audit value
FSI	S/H	BNS / AE		large variability
	FD	TXW / Bt	30113–25,6	large variability
		TXW / Bt	30126–18,23	large variability
	PD	TWD / C	30112–37,18	large variability
	AS	C	30118–6	high field audit value
		B	30106–4,11	high lab audit value
		B	30106–3,34	low field audit value
		Bw	30109–23,26	low lab audit value
		Bw	30115–10,28	low field audit value
CLAY	S/H	BXP / Bw		high value
		TXW / Bw		high value
	PD	CFP / C	30115–30,31	large variability
	AS	C	30118–6	high field audit value
		Bw	30109–23,26	high lab audit values
PH_H2O	S/H	FLW / BA		high value
		BNS / Oe		large variability *
	FD	TXW / Btx	30108–39,10	large variability
	PD	TXW / Btx	30108–39,6	large variability
	AS	Bw	30107–27,36	high field audit value
PH_002M	S/H	FLW / BA		high value
		BNS / Cr		large variability
		BNS / Oe		large variability *
	FD	BMD / Bw	30105–39,3	high value
		TXW / Bt	30113–25,6	large variability
	PD	BMD / Bw	30105–3,7	high FD value
	AS	Bw	30107–12,37	high lab audit value
		C	30108–19	low lab audit value
PH_01M	S/H	FLW / BA		high value
		BNS / Oe		large variability *
	FD	TXW / Bt	30113–25,6	large variability
		BMD / E	30118–4,17	large variability
		BND / Bw	30123–34,4	large variability
	AS	Bw	30119–20,33	high field audit value
		C	30104–40	low lab audit value
CA_CL	S/H	BNS / Oe		high value
		FLW / Ap		large variability
	FD	TXW / Bt	30113–25,6	high value
		FLW / C	30120–34,32	large variability
		BXW / Bw	30128–34,16	large variability
	PD	TPD / Bt	30114–8,18	large variability
		TPD / Bt	30114–21,1	large variability
	AS	O	30131–6,13,31	high lab audit value
MG_CL	S/H	BNS / Oe		large variability
		TPD / Bw		large variability
	FD	HST / Oe	30131–14,19	large variability
	AS	B	30122–6,28	high lab audit value
		B	30128–7,24	high field audit values
		O	30131–6,13,31	large lab audit variability

(Continued)

Table D-1. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
K_CL	S/H	FLW / Ap		large variability
	FD	TXW / Bt	30113–25,6	large variability
	PD	BMK / C	30107–25,34	large variability
		HST / Oe	30131–19,24	large variability
	AS	O	30131–6,13,31	large lab audit variability
NA_CL	FD	FLW / C	30120–34,32	large variability
	PD	FLW / C	30120–34,38	large variability
	AS	Bw	30107–12,37	high lab audit value
		B	30104–19,38	high lab audit value
		B	30110–29,39	large field audit variability
		B	30116–7,22	low field audit value
AL_CL	S/H	TXW / Oe		large variability
	FD	HST / Oe	30132–26,39	large variability
		BMD / Ap	30104–29,14	large variability
	AS	B	30122–6,28	low lab audit value
		B	30120–10,37	low lab audit value
CA_OAC	S/H	BMK / Oe		large variability
		BNS / Oe		high value
		FLW / Ap		large variability
	FD	TXW / Bt	30113–25,6	high value
		BMD / Ap	30104–29,14	large variability
		FLW / C	30120–34,32	large variability
		FLW / Cg	30121–1,19	large variability
		BXW / Bw	30128–34,16	large variability
		HST / Oe	30132–26,39	large variability
	PD	TPD / Bt	30114–8,18	high value
		HST / Oe	30131–19,24	large variability
	AS	C	30113–5	high lab audit value
		B	30128–7,24	high field audit value
		B	30126–4,35	high field audit value
		Bw	30115–18,36	high lab audit value
MG_OAC	S/H	TPD / Bw		large variability
		BNS / Oe		large variability
		TPD / C		large variability
	FD	TPD / Bt	30114–8,21	large variability
		TXW / Bt	30126–18,23	high value
	PD	BMK / C	30107–6,1	large variability
		HST / Oe	30131–19,24	large variability
	AS	Bw	30105–32,34	high field audit value
		Bw	30115–18,36	high lab audit value
		B	30122–6,28	high lab audit value
		B	30128–7,24	high field audit value
K_OAC	S/H	FLW / Ap		large variability
		FLW / BA		large variability
	FD	HST / Oe	30131–14,19	large variability
	PD	HST / Oe	30131–19,24	large variability
	AS	C	30112–38	high field audit value
		Bw	30125–3,27	high lab audit value
NA_OAC	S/H	BMD / A		large variability *
	FD	TPD / Bt	30114–8,21	high value
		TXP / Btx	30125–29,1	large variability
	PD	TPD / Bt	30114–8,18	high value
		TXP / Btw	30125–1,26	large variability
		HST / Oe	30131–19,24	low value
	AS	C	30123–38	high field audit value
		Bw	30115–18,36	high lab audit value
		Bw	30129–2,31	high lab audit value

(Continued)

Table D-1. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
CEC_CL	S/H	BNS / Oe		large variability
	FD	TXW / Bt	30113-25,6	large variability
	PD	TWM / C	30127-7,34	high value
		TWM / C	30127-5,8	high value
		BXP / Bx	30130-35,4	large variability
	AS	B	30108-9,27	low field audit value
		B	30112-8,24	large field audit variability
		B	30114-16,26	high lab audit value
CEC_OAC	FD	BND / Bw	30106-25,24	large variability
	PD	BND / Bw	30106-24,5	large variability
		TXW / A	30119-2,13	high value
		HST / Oe	30131-19,24	low value
	AS	O	30132-14,17,31	low field audit value
AC_BACL	FD	BMD / Ap	30104-29,14	large variability
		TXW / A	30119-2,8	large variability
		FLW / Bw	30124-7,34	large variability
	PD	TXW / A	30119-2,13	large variability
	AS	C	30105-37	high field audit value
		Bw	30117-5,32	high field audit value
CA_CL2	FD	HST / Oe	30131-14,19	large variability
	PD	TXW / A	30119-8,35	large variability
	AS	C	30119-19	low lab audit value
		Bw	30119-20,33	large field audit variability
		Bw	30125-24,37	high field audit value
MG_CL2	PD	BMK / C	30107-6,1	large variability
		TXW / A	30119-8,35	low value
		HST / Oe	30131-14,3	large variability
	AS	B	30128-13,29	low lab audit value
		B	30128-7,24	high field audit value
		Bw	30119-20,33	large field audit variability
K_CL2	S/H	FLW / Ap		large variability
		FLW / BA		large variability
	FD	HST / Oe	30132-26,39	large variability
	PD	TWD / C	30112-37,18	high value
		CFP / C	30115-39,6	high value
	AS	C	30130-31	high lab audit value
NA_CL2	AS	B	30122-6,28	low lab audit value
		B	30128-13,29	low lab audit value
FE_CL2	S/H	BXP / A		large variability
		BXP / Oe		large variability
		CMS / C		large variability
		TXP / Ap		large variability
	FD	TXW / A	30119-2,8	large variability
		HST / Oe	30132-26,39	large variability
AL_CL2	S/H	CMS / C		large variability
		TXW / Bx		high value
		TXW / Oe		large variability
	FD	TXW / Bt	30113-25,6	large variability
		FLW / C	30120-34,32	large variability
	PD	TXW / A	30119-8,35	large variability
		BXW / Bw	30122-19,36	large variability
	AS	Bw	30113-1,23	high lab audit value
		O	30131-6,13,31	large lab audit variability

(Continued)

Table D-1. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
FE_PYP	S/H	BXP / A		large variability *
		BXP / Bw		high value
	AS	Bw	30109–29,36	high field audit value
		Bw	30125–24,37	low field audit value
AL_PYP	S/H	BXP / Bx		high value
		BXP / C		high value
		TXW / Oe		large variability
	AS	Bw	30125–3,27	large lab audit variability
FE_AO	FD	TXW / Bt	30126–18,23	low value
		CFP / C	30115–39,30	large variability
		HST / Oe	30132–26,39	large variability
	PD	TXW / Bt	30126–23,5	low value
	AS	C	30106–14	high field audit value
		C	30129–36	high lab audit value
		Bw	30105–20,38	large lab audit variability
		Bw	30121–3,35	large lab audit variability
AL_AO	S/H	TXW / Oe		large variability
	FD	TXW / Bt	30126–18,23	low value
		FLW / C	30120–34,32	high value
	PD	TXW / Bt	30126–23,5	low value
		BND / Bw	30123–4,11	large variability
	AS	Bw	30125–24,37	low field audit value
		B	30120–10,37	high lab audit value
SI_AO	S/H	FLW / BC		large variability
		BMK / Bhs		large variability
	FD	FLW / C	30120–34,32	large variability
	PD	CFP / C	30115–39,6	large variability
	AS	Bw	30121–3,35	high lab audit value
		Bw	30121–4,21	high field audit value
		B	30124–13,35	high lab audit value
FE_CD	S/H	TXP / C		large variability
	FD	TWD / Bt	30109–14,30	large variability
	PD	TWD / Bt	30109–30,38	low value
	AS	Bw	30109–29,36	low lab audit value
AL_CD	S/H	BMK / Bhs		large variability
		TXW / Oe		large variability
	FD	FLW / C	30120–34,32	large variability
	PD	BMD / Ap	30104–14,31	large variability
		TWD / Bt	30109–30,38	low value
	AS	B	30110–2,38	large lab audit variability
SO4_H2O	S/H	CMS / C		high value
		HST / Oe		large variability
		TPD / Bt		large variability
	FD	BND / Bw	30123–34,4	large variability
		TXP / Btx	30125–29,1	high value
		HST / Oe	30132–26,39	high value
	PD	BND / Bw	30123–4,11	large variability
		TXP / Btx	30125–29,8	high value
		HST / Oe	30132–26,34	large variability
	AS	C	30106–9	low lab audit value
		B	30114–16,26	low lab audit value
		Bw	30119–11,34	high lab audit value
		Bw	30125–24,37	low field audit value
		O	30132–2,6,28	large lab audit variability

(Continued)

Table D-1. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
SO4_PO4	S/H	CMS / C		high value
	FD	TXW / Bt	30113–25,6	large variability
		FLW / C	30120–34,32	large variability
	PD	BND / Bw	30106–24,5	large variability
		BMK / C	30107–6,1	large variability
		TXP / Btx	30125–1,26	large variability
	AS	B	30122–6,28	low lab audit value
		B	30124–4,21	high field audit value
SO4_0	S/H	CMS / C		high value
	AS	C	30122–8	high lab audit value
		Bw	30119–20,33	large field audit variability
SO4_2	S/H	CMS / C		high value
	AS	Bw	30115–10,28	low field audit value
SO4_4	S/H	CMS / C		high value
	FD	TXW / Bt	30113–25,6	large variability
		FLW / Bw	30124–7,34	low value
	PD	TXW / A	30119–8,35	large variability
		FLW / Bw	30124–34,32	large variability
	AS	Bw	30105–32,34	high field audit value
SO4_8	S/H	CMS / C		high value
		/ BC		large variability
	FD	TXW / Bt	30113–25,6	large variability
	AS	Bw	30109–29,36	low field audit value
SO4_16	S/H	CMS / C		high value
		/ BC		large variability
	PD	BND / Bw	30111–32,13	large variability
		TWM / C	30127–7,34	low value
	AS	B	30128–7,24	low field audit value
		Bw	30111–14,39	high lab audit value
		Bw	30113–1,23	high field audit value
SO4_32	S/H	CMS / C		high value
		/ BC		large variability
	FD	TXW / Bt	30126–18,23	low value
	PD	TWD / Bt	30109–14,20	high value
		FLW / C	30120–34,38	large variability
		TXW / Bt	30126–23,5	low value
	AS	C	30122–31	low field audit value
		Bw	30111–14,29	low lab audit value
		B	30110–29,39	large field audit variability
		B	30128–7,24	low field audit value
C_TOT	S/H	CMS / C		large variability
		TXW / A		large variability *
	FD	BMD / Ap	30104–29,14	large variability
		BMD / E	30118–4,17	large variability
		TXW / A	30119–2,8	large variability
	PD	BXW / Bw	30128–18,34	large variability
		HST / Oe	30131–3,14	large variability
	AS	B	30120–10,37	high lab audit value
N_TOT	FD	TXW / A	30119–2,8	large variability
	AS	Bw	30121–3,35	low lab audit value

Table D-1. Continued

Parameter	Data set[a]	Sampling class/horizon	Batch/sample	Reason
S_TOT	S/H	CMS / C		large variability
		HST / Oe		large variability
		TXW / A		large variability *
	AS	C	30107–8	high field audit value
		B	30114–16,26	low lab audit value
		Bw	30113–1,23	low lab audit value

[a] S/H = sampling class/horizon groups of routine samples; FD = field duplicates; PD = preparation duplicates; AS audit samples.

* Organic soil sample included.

Appendix E

Precision Plots for Particle Size Fractions

Following are precision plots for the routine and QA data sets from the VCOS, COS, MS, FS, VFS, COSI, and FSI parameters. Since these parameters did not have specifically established DQOs, it was decided to place the routine data plots in the appendix and separate from the audit sample/routine sample paired plots found Section 3 in the Results and Discussion of the report. Supplemental information relating to these plots can be found in Section 3 under the parameter group heading and in Appendices C and D.

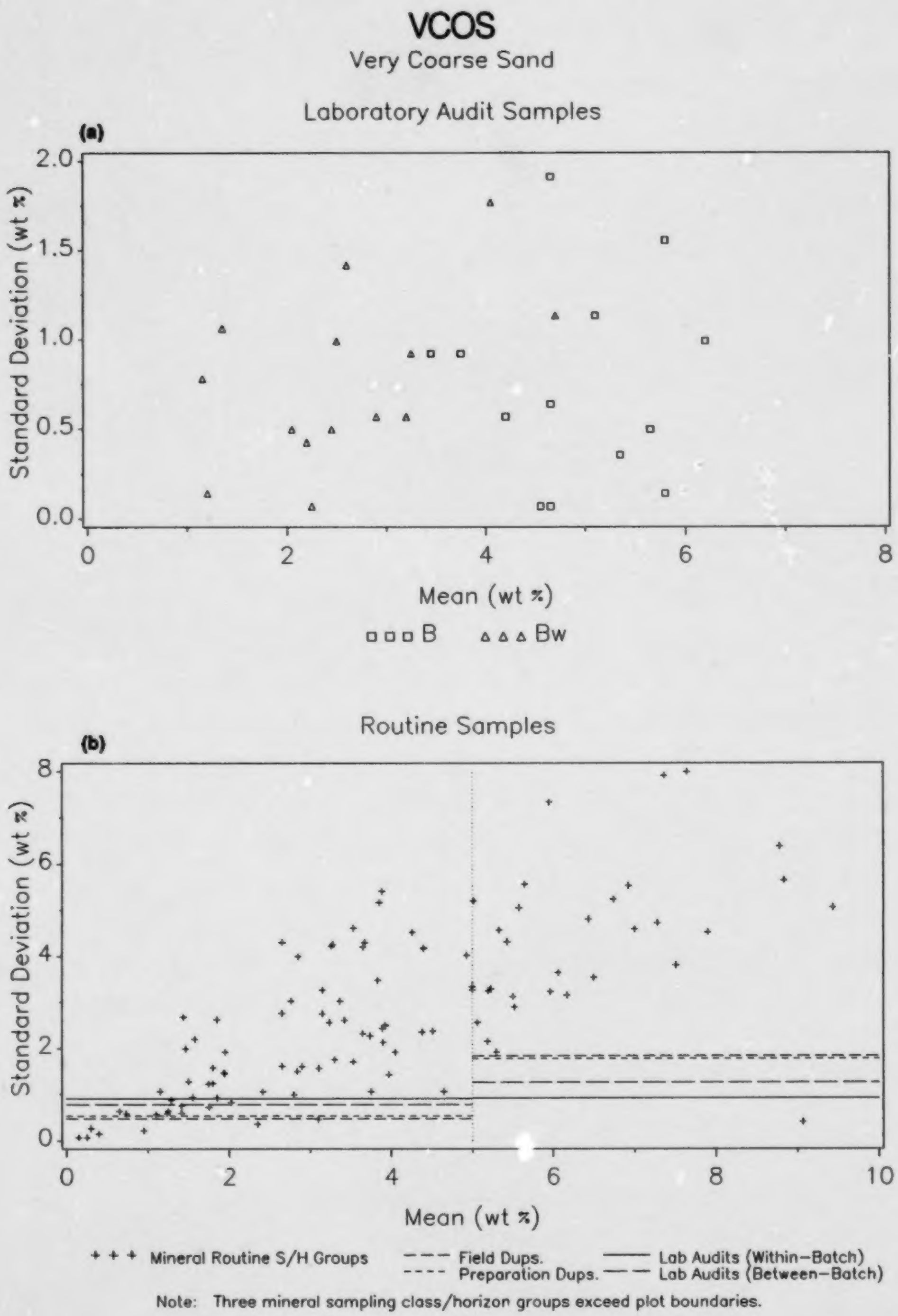
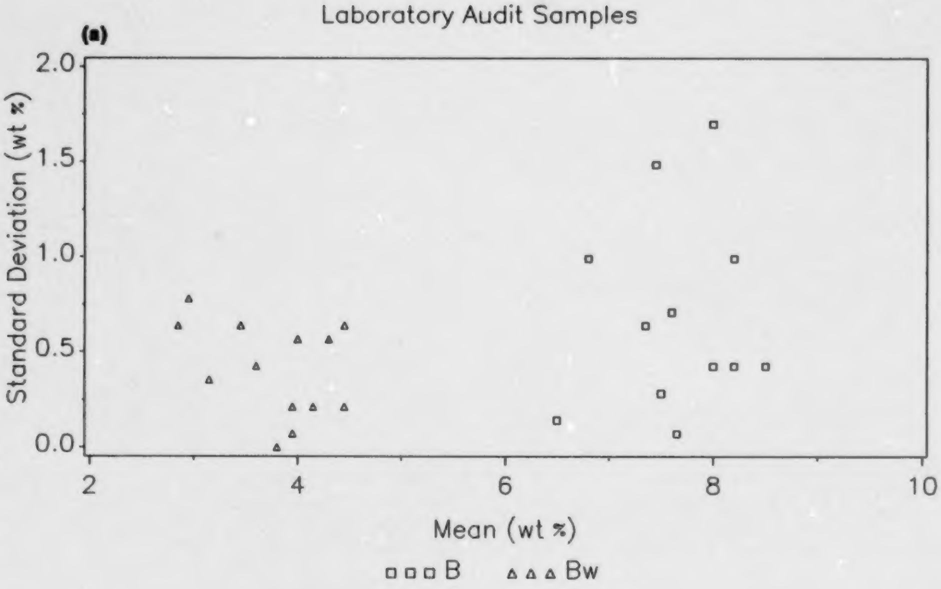


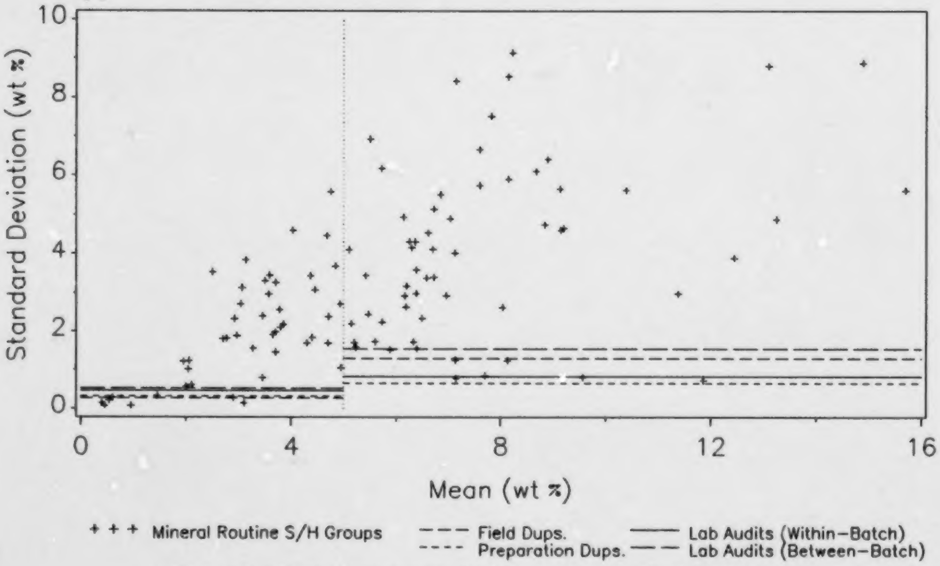
Figure E-1. Range and frequency distribution of VCOS for: (a) laboratory audit samples and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

COS
Coarse Sand

Laboratory Audit Samples

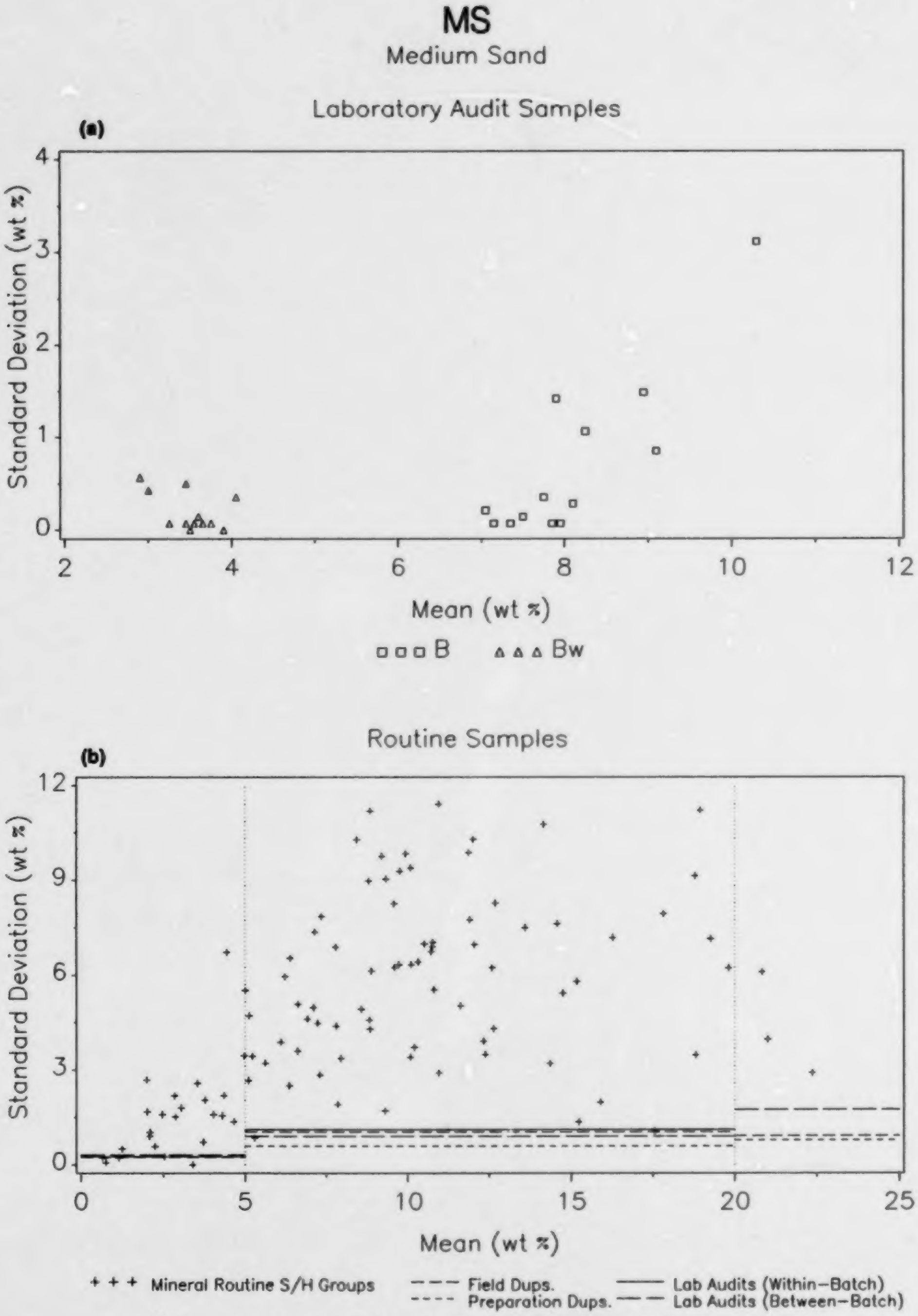


Routine Samples



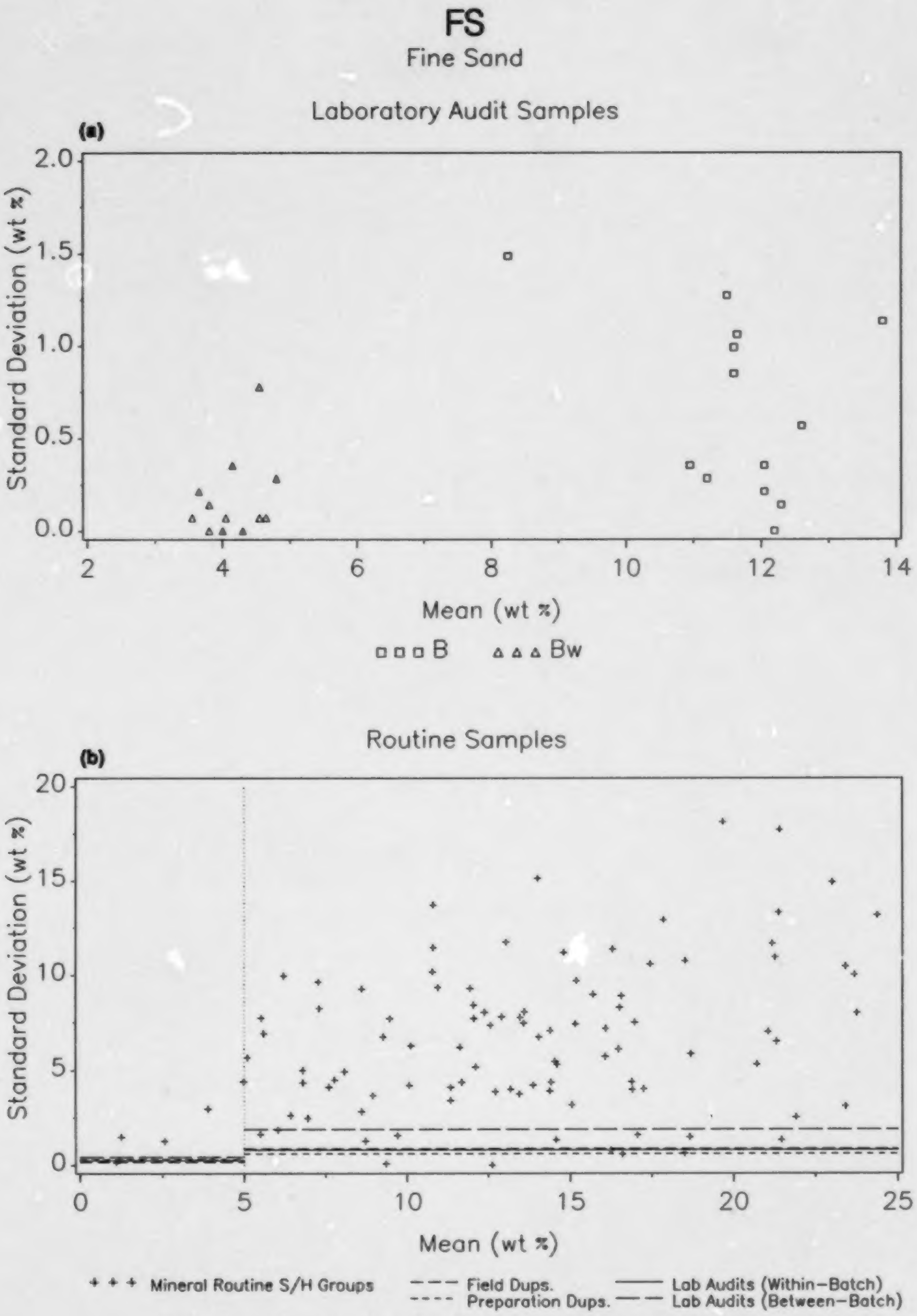
Note: One mineral sampling class/horizon groups exceed plot boundaries.

Figure E-2. Range and frequency distribution of COS for: (a) laboratory audit samples and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



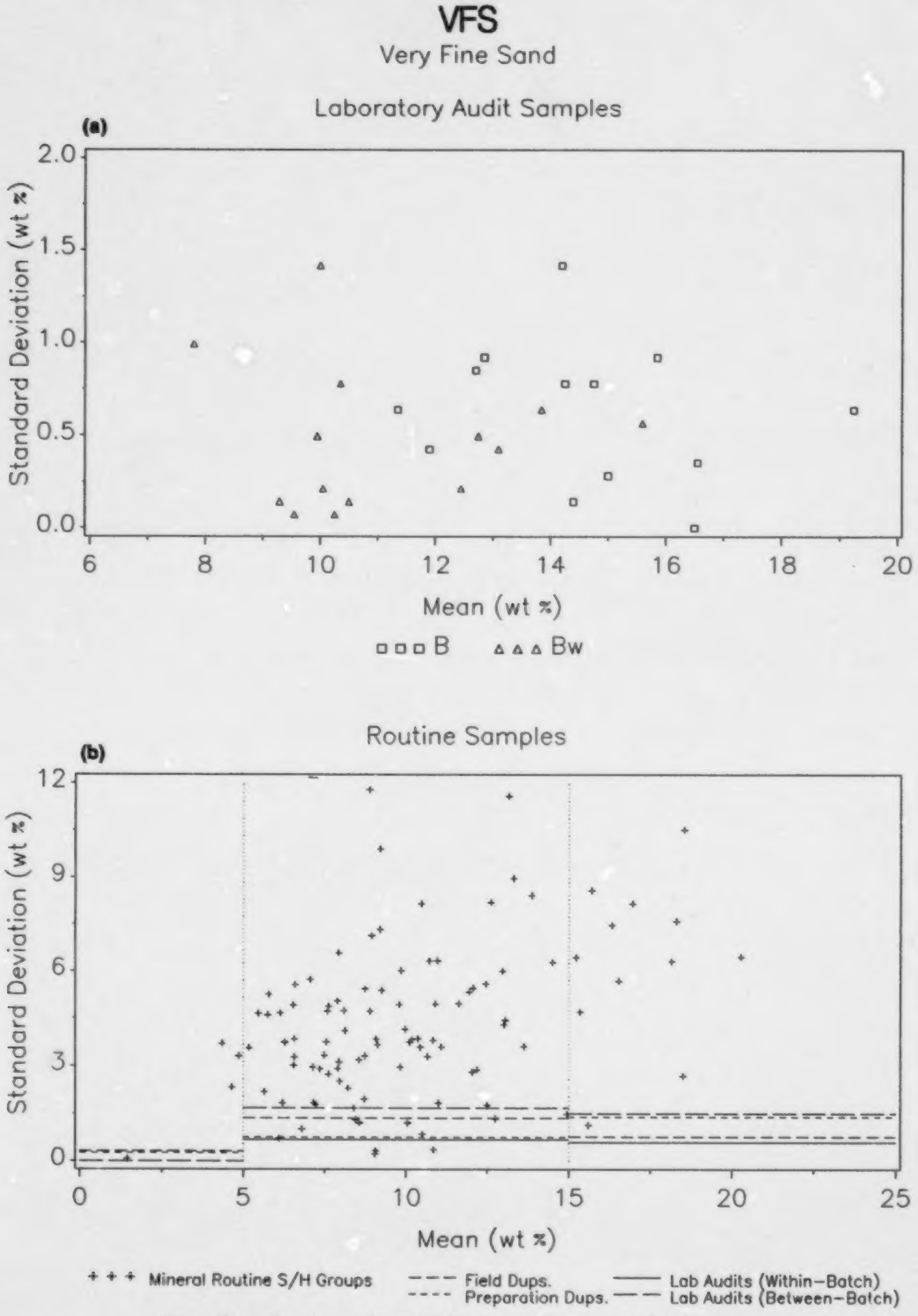
Note: Four mineral sampling class/horizon groups exceed plot boundaries.

Figure E-3. Range and frequency distribution of MS for: (a) laboratory audit samples and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.



Note: Four mineral sampling class/horizon groups exceed plot boundaries.

Figure E-4. Range and frequency distribution of FS for: (a) laboratory audit samples and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

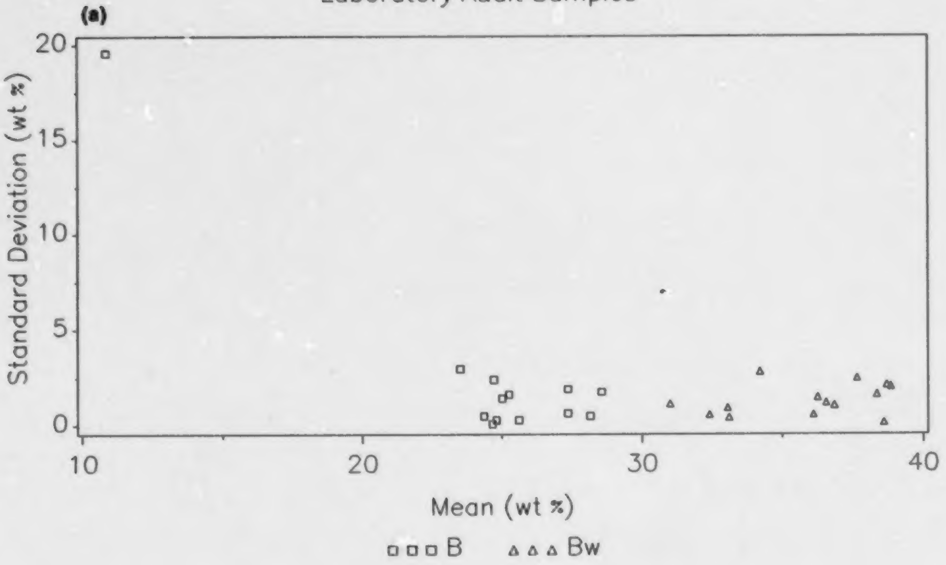


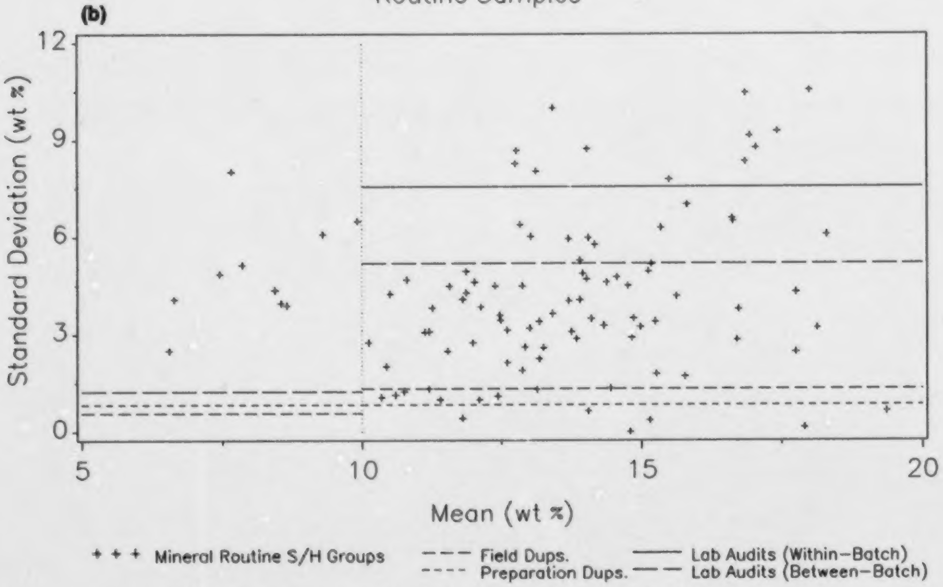
Note: Two mineral sampling class/horizon groups exceed plot boundaries.

Figure E-5. Range and frequency distribution of VFS for: (a) laboratory audit samples and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

COSI

Coarse Silt


Laboratory Audit Samples


Routine Samples

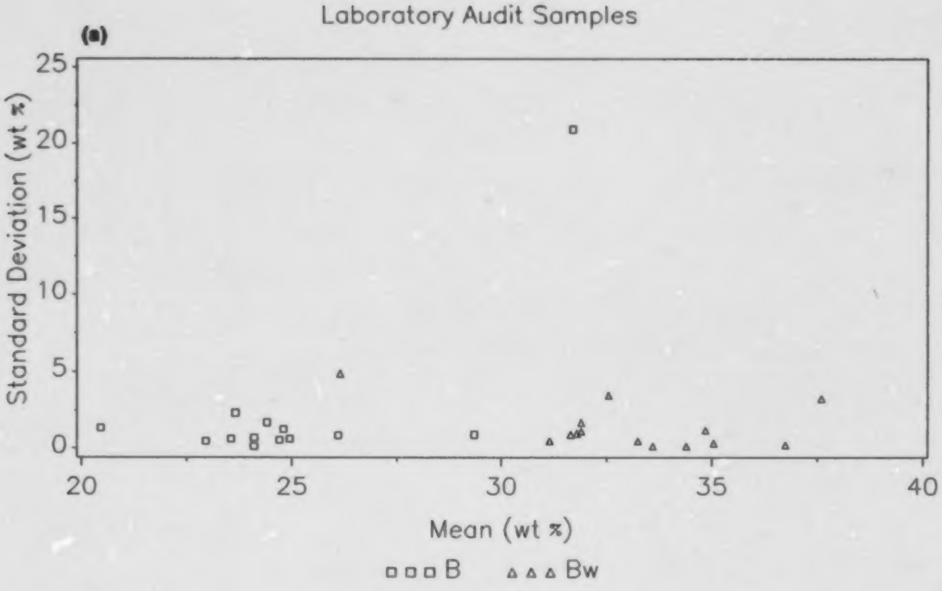
Note: Five mineral sampling class/horizon groups exceed plot boundaries.

Figure E-6. Range and frequency distribution of COSI for: (a) laboratory audit samples and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

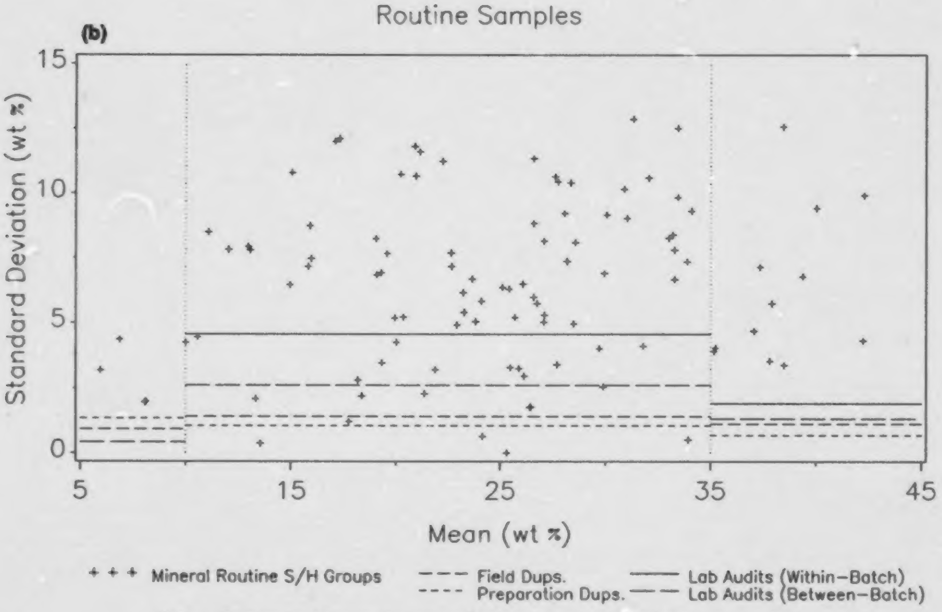
FSI

Fine Silt

Laboratory Audit Samples



Routine Samples



Note: Three mineral sampling class/horizon groups exceed plot boundaries.

Figure E-7. Range and frequency distribution of FSI for: (a) laboratory audit samples and (b) sampling class/horizon routine sample data partitioned into concentration intervals of uniform variability and their relation to pooled precision estimates.

Appendix F

General Statistics for the Laboratory Audit Samples

Appendix F is a summary table of the soil chemistry and physical data for the laboratory audit samples. Included are the data sorted by laboratory and by audit sample type for number of samples (n), mean concentration, and standard deviation. Supplemental information relating to this table can be found in the precision discussion and figures in Sections 2 and 3 of the report. Data are presented for each of the 50 analytical parameters in the order described in Table 1-1 of Section 1 of the report.

Table F-1. Summary Statistics of Analytical Parameters for Laboratory Audit Samples

	Audit Sample[a]											
	B			Bw			C			O		
Laboratory	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
Air Dry Moisture Percent (MOIST) wt. %												
1	10	5.01	0.19	8	2.57	0.12	9	0.12	0.04	–[b]	–	–
2	8	5.25	0.31	10	2.35	0.20	9	0.12	0.12	–	–	–
4	8	5.25	0.22	10	2.53	0.19	9	0.14	0.05	6	7.56	0.63
Total Sand (SAND) 2.0 - 0.05 mm wt. %												
1	10	46.73	1.31	8	23.96	0.87	9	96.21	0.98	–	–	–
2	8	49.81	3.34	10	28.47	1.32	9	97.30	0.71	–	–	–
4	8	44.16	2.80	10	22.48	3.21	9	96.91	1.45	–	–	–
Very Coarse Sand (VCOS) 2.0 - 1.0 mm wt. %												
1	10	4.95	0.96	8	2.54	0.63	9	5.62	1.29	–	–	–
2	8	5.15	0.92	10	3.05	1.04	9	5.06	1.03	–	–	–
4	8	4.61	1.33	10	2.09	1.54	9	6.30	2.31	–	–	–
Coarse Sand (COS) 1.0 - 0.5 mm wt. %												
1	10	7.87	0.61	8	4.14	0.39	9	16.97	1.45	–	–	–
2	8	7.20	0.98	10	3.92	0.35	9	15.82	1.32	–	–	–
4	8	7.74	0.80	10	3.37	0.74	9	17.74	4.90	–	–	–
Medium Sand (MS) 0.5 - 0.25 mm wt. %												
1	10	7.80	0.31	8	3.46	0.16	9	33.13	0.78	–	–	–
2	8	7.85	1.08	10	3.65	0.24	9	33.04	2.12	–	–	–
4	8	8.70	1.77	10	3.44	0.53	9	32.92	2.21	–	–	–
Fine Sand (FS) 0.25 - 0.1 mm wt. %												
1	10	11.57	0.69	8	3.69	0.22	9	30.88	1.64	–	–	–
2	8	12.59	0.87	10	4.33	0.28	9	34.61	1.72	–	–	–
4	8	10.89	1.89	10	4.20	0.51	9	31.79	4.87	–	–	–
Very Fine Sand (VFS) 0.1 - 0.05 mm wt. %												
1	10	14.52	0.69	8	10.19	0.31	9	9.66	1.74	–	–	–
2	8	17.04	1.47	10	13.55	1.24	9	8.78	1.63	–	–	–
4	8	12.20	0.86	10	9.40	1.12	9	8.20	2.31	–	–	–
Total Silt (SILT) 0.05 - 0.002 mm wt. %												
1	10	49.87	1.19	8	70.15	0.96	9	3.70	0.95	–	–	–
2	8	45.90	3.41	10	63.90	4.25	9	2.30	0.77	–	–	–
4	8	52.99	1.69	10	72.83	2.81	9	3.01	1.41	–	–	–
Coarse Silt (COSI) 0.02 - 0.005 mm wt. %												
1	10	25.53	1.18	8	37.48	1.35	9	3.46	0.95	–	–	–
2	8	20.92	9.77	10	32.75	1.55	9	1.89	0.70	–	–	–
4	8	27.19	2.10	10	37.60	1.82	9	2.61	1.47	–	–	–
Fine Silt (FSI) 0.02 - 0.005 mm wt. %												
1	10	24.34	0.84	8	32.67	1.50	9	0.24	0.16	–	–	–
2	8	24.97	9.11	10	31.15	3.41	9	0.41	0.21	–	–	–
4	8	25.80	2.62	10	35.23	2.40	9	0.40	0.68	–	–	–

(Continued)

Table F-1. Continued

	Audit Sample[a]											
	B			Bw			C			O		
Laboratory	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
Total Clay (CLAY) < 0.002 mm wt. %												
1	10	3.40	0.47	8	5.89	0.41	9	0.09	0.09	–	–	–
2	8	4.29	1.12	10	7.63	3.22	9	0.40	0.30	–	–	–
4	8	2.85	1.31	10	4.69	0.93	9	0.08	0.08	–	–	–
pH in Water (PH_H2O) pH units												
1	10	4.92	0.06	8	5.13	0.09	9	5.30	0.11	–	–	–
2	8	4.91	0.03	10	5.09	0.07	9	5.47	0.07	–	–	–
4	8	4.85	0.05	10	5.07	0.08	9	5.18	0.08	6	4.06	0.03
pH in 0.002M Calcium Chloride (PH_002M) pH units												
1	10	4.49	0.04	8	4.79	0.11	9	4.99	0.18	–	–	–
2	8	4.49	0.02	10	4.76	0.04	9	5.17	0.05	–	–	–
4	8	4.35	0.02	10	4.69	0.05	9	4.89	0.36	6	3.63	0.01
pH in 0.01M Calcium Chloride (PH_01M) pH units												
1	10	4.32	0.06	8	4.55	0.04	9	4.75	0.07	–	–	–
2	8	4.25	0.05	10	4.55	0.04	9	4.79	0.05	–	–	–
4	8	4.28	0.05	10	4.60	0.04	9	4.72	0.07	6	3.33	0.02
Calcium in Ammonium Chloride (CA_CL) meq/100g												
1	10	0.36	0.03	8	0.26	0.03	9	0.10	0.04	–	–	–
2	8	0.36	0.03	10	0.26	0.01	9	0.06	0.01	–	–	–
4	8	0.35	0.03	10	0.27	0.01	9	0.06	0.01	6	11.39	0.51
Magnesium in Ammonium Chloride (MG_CL) meq/100g												
1	10	0.09	0.02	8	0.07	0.02	9	0.03	0.01	–	–	–
2	8	0.08	0.01	10	0.05	0.00	9	0.02	0.00	–	–	–
4	8	0.09	0.01	10	0.06	0.00	9	0.03	0.00	[illegible]	3.09	0.13
Potassium in Ammonium Chloride (K_CL) meq/100g												
1	10	0.08	0.01	8	0.06	0.01	9	0.03	0.01	–	–	–
2	8	0.09	0.00	10	0.07	0.00	9	0.03	0.00	–	–	–
4	8	0.09	0.00	10	0.06	0.00	9	0.03	0.00	6	1.13	0.06
Sodium in Ammonium Chloride (NA_CL) meq/100g												
1	10	0.06	0.02	8	0.02	0.01	9	0.01	0.01	–	–	–
2	8	0.06	0.00	10	0.03	0.00	9	0.00	0.00	–	–	–
4	8	0.07	0.01	10	0.03	0.00	9	0.01	0.00	6	0.43	0.01
Aluminum in Ammonium Chloride (AL_CL) meq/100g												
1	10	3.29	0.91	8	1.62	0.11	9	0.24	0.14	–	–	–
2	8	3.74	0.25	10	1.80	0.12	9	0.17	0.02	–	–	–
4	8	3.42	0.34	10	1.96	0.09	9	0.21	0.03	6	5.90	0.13
Calcium in Ammonium Acetate (CA_OAC) meq/100g												
1	10	0.29	0.03	8	0.25	0.01	9	0.10	0.03	–	–	–
2	8	0.27	0.01	10	0.26	0.05	9	0.06	0.02	–	–	–
4	8	0.30	0.03	10	0.24	0.01	9	0.05	0.01	6	8.30	0.28

(Continued)

Table F-1. Continued

Laboratory	Audit Sample[a]											
	B			Bw			C			O		
	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
				Magnesium in Ammonium Acetate (MG_OAC) meq/100g								
1	10	0.09	0.02	8	0.05	0.01	9	0.04	0.01	–	–	–
2	8	0.08	0.01	10	0.06	0.02	9	0.03	0.01	–	–	–
4	8	0.09	0.01	10	0.05	0.01	9	0.02	0.00	6	2.63	0.11
				Potassium in Ammonium Acetate (K_OAC) meq/100g								
1	10	0.09	0.01	8	0.06	0.01	9	0.03	0.01	–	–	–
2	8	0.09	0.00	10	0.06	0.00	9	0.03	0.00	–	–	–
4	8	0.09	0.00	10	0.06	0.00	9	0.02	0.00	6	1.12	0.03
				Sodium in Ammonium Acetate (NA_OAC) meq/100g								
1	10	0.06	0.01	8	0.03	0.00	9	0.01	0.00	–	–	–
2	8	0.06	0.00	10	0.03	0.01	9	0.01	0.00	–	–	–
4	8	0.07	0.00	10	0.03	0.01	9	0.01	0.00	6	0.45	0.01
				Cation Exchange Capacity-Ammonium Chloride (CEC_CL) meq/100g								
1	10	7.16	0.27	8	4.61	0.19	9	0.60	0.06	–	–	–
2	8	7.48	0.27	10	4.23	0.14	9	0.71	0.13	–	–	–
4	8	7.56	0.83	10	4.44	0.33	9	0.50	0.07	6	26.30	0.87
				Cation Exchange Capacity-Ammonium Acetate (CEC_OAC) meq/100g								
1	10	23.47	1.45	8	11.96	1.61	9	1.07	0.09	–	–	–
2	8	20.51	0.69	10	9.89	0.26	9	0.98	0.23	–	–	–
4	8	23.81	2.25	10	11.30	0.63	9	0.87	0.08	6	82.72	1.01
				Barium Chloride-TEA Acidity (AC_BACL) meq/100g								
1	10	27.22	1.57	8	15.36	0.91	9	1.04	0.66	–	–	–
2	8	28.02	1.90	10	16.02	2.17	9	0.59	0.76	–	–	–
4	8	32.26	1.59	10	17.33	0.85	9	1.01	0.27	6	107.38	2.73
				Calcium in Calcium Chloride (CA_CL2) meq/100g								
1	10	0.55	0.03	8	0.59	0.06	9	0.76	0.06	–	–	–
2	8	0.50	0.02	10	0.59	0.03	9	0.76	0.03	–	–	–
4	8	0.52	0.01	10	0.63	0.01	9	0.76	0.01	6	1.48	0.03
				Magnesium in Calcium Chloride (MG_CL2) meq/100g								
1	10	0.06	0.01	8	0.04	0.00	9	0.02	0.01	–	–	–
2	8	0.06	0.00	10	0.03	0.01	9	0.02	0.01	–	–	–
4	8	0.06	0.00	10	0.04	0.00	9	0.02	0.00	6	0.69	0.01
				Potassium in Calcium Chloride (K_CL2) meq/100g								
1	10	0.02	0.00	8	0.01	0.00	9	0.01	0.00	–	–	–
2	8	0.03	0.00	10	0.01	0.00	9	0.01	0.00	–	–	–
4	8	0.02	0.00	10	0.01	0.00	9	0.01	0.00	6	0.60	0.01
				Sodium in Calcium Chloride (NA_CL2) meq/100g								
1	10	0.05	0.01	8	0.02	0.00	9	0.01	0.00	–	–	–
2	8	0.05	0.00	10	0.02	0.00	9	0.00	0.00	–	–	–
4	8	0.05	0.00	10	0.02	0.00	9	0.00	0.00	6	0.31	0.01

(Continued)

Table F-1. Continued

	Audit Sample*											
	B			Bw			C			O		
Laboratory	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
Iron in Calcium Chloride (FE_CL2) meq/100g												
1	10	0.00	0.00	8	0.00	0.00	9	0.00	0.00	–	–	–
2	8	0.00	0.00	10	0.00	0.00	9	0.00	0.00	–	–	–
4	8	0.01	0.00	10	0.00	0.00	9	0.00	0.00	6	0.02	0.00
Aluminum in Calcium Chloride (AL_CL2) meq/100g												
1	10	0.06	0.02	8	0.01	0.01	9	0.01	0.01	–	–	–
2	8	0.05	0.01	10	0.00	0.00	9	0.00	0.00	–	–	–
4	8	0.06	0.00	10	0.01	0.00	9	0.01	0.00	6	0.27	0.01
Pyrophosphate-Extractable Iron (FE_PYP) wt. %												
1	10	0.65	0.05	8	0.78	0.05	9	0.03	0.01	–	–	–
2	8	0.62	0.03	10	0.79	0.06	9	0.04	0.01	–	–	–
4	8	0.61	0.02	10	0.71	0.03	9	0.04	0.01	6	0.10	0.00
Pyrophosphate-Extractable Aluminum (AL_PYP) wt. %												
1	10	0.89	0.07	8	0.53	0.06	9	0.07	0.01	–	–	–
2	8	0.81	0.04	10	0.57	0.04	9	0.05	0.01	–	–	–
4	8	0.81	0.04	10	0.51	0.02	9	0.06	0.01	6	0.23	0.00
Acid Oxalate-Extractable Iron (FE_AO) wt. %												
1	10	0.96	0.06	8	1.02	0.13	9	0.06	0.01	–	–	–
2	8	1.03	0.09	10	1.00	0.10	9	0.05	0.02	–	–	–
4	8	0.96	0.03	10	0.99	0.07	9	0.08	0.06	6	0.14	0.01
Acid Oxalate-Extractable Aluminum (AL_AO) wt. %												
1	10	1.39	0.09	8	0.87	0.05	9	0.08	0.02	–	–	–
2	8	1.37	0.05	10	0.88	0.04	9	0.07	0.02	–	–	–
4	8	1.45	0.06	10	0.87	0.06	9	0.07	0.01	6	0.26	0.01
Acid Oxalate-Extractable Silicon (SI_AO) wt. %												
1	10	0.27	0.03	8	0.16	0.02	9	0.02	0.01	–	–	–
2	8	0.40	0.05	10	0.26	0.05	9	0.03	0.01	–	–	–
4	8	0.31	0.02	10	0.20	0.02	9	0.03	0.01	6	0.01	0.00
Citrate Dithionite-Extractable Iron (FE_CD) wt. %												
1	10	1.38	0.15	8	1.76	0.13	9	0.16	0.03	–	–	–
2	8	1.46	0.07	10	1.77	0.09	9	0.15	0.05	–	–	–
4	8	1.46	0.07	10	1.69	0.03	9	0.15	0.01	6	0.23	0.00
Citrate Dithionite-Extractable Aluminum (AL_CD) wt. %												
1	10	1.06	0.11	8	0.61	0.04	9	0.06	0.01	–	–	–
2	8	1.14	0.13	10	0.67	0.04	9	0.05	0.01	–	–	–
4	8	1.16	0.08	10	0.62	0.01	9	0.06	0.01	6	0.26	0.00
Water-Extractable Sulfate (SO4_H20) mg S/kg												
1	10	13.40	1.35	8	20.08	3.28	9	3.05	0.51	–	–	–
2	8	13.00	0.81	10	20.80	1.04	9	2.36	1.20	–	–	–
4	8	13.13	3.31	10	20.53	0.96	9	2.67	0.53	6	44.17	2.63

(Continued)

Table F-1. Continued

	Audit Sample[a]											
	B			Bw			C			O		
Laboratory	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
Phosphate-Extractable Sulfate (SO4_PO4) mg S/kg												
1	10	78.80	20.12	8	115.55	2.69	9	4.96	2.04	–	–	–
2	8	71.31	6.35	10	114.39	7.38	9	5.34	1.77	–	–	–
4	8	78.31	2.78	10	100.99	3.56	9	4.96	1.67	6	47.64	2.45
0 mg S/L Isotherm Parameter (SO4_0) mg S/L												
1	10	1.30	0.09	8	2.06	0.11	9	0.53	0.13	–	–	–
2	8	1.25	0.08	10	2.14	0.12	9	0.46	0.09	–	–	–
4	8	1.29	0.10	10	2.10	0.07	9	0.42	0.11	–	–	–
2 mg S/L Isotherm Parameter (SO4_2) mg S/L												
1	10	2.24	0.05	8	3.10	0.11	9	2.51	0.11	–	–	–
2	8	2.12	0.13	10	3.12	0.06	9	2.37	0.15	–	–	–
4	8	2.05	0.08	10	3.16	0.11	9	2.37	0.15	–	–	–
4 mg S/L Isotherm Parameter (SO4_4) mg S/L												
1	10	3.28	0.11	8	4.29	0.12	9	4.42	0.09	–	–	–
2	8	3.22	0.10	10	4.24	0.11	9	4.40	0.20	–	–	–
4	8	3.03	0.11	10	4.07	0.15	9	4.22	0.13	–	–	–
8 mg S/L Isotherm Parameter (SO4_8) mg S/L												
1	10	5.43	0.14	8	6.55	0.13	9	8.39	0.26	–	–	–
2	8	5.29	0.25	10	6.44	0.12	9	8.21	0.14	–	–	–
4	8	4.91	0.47	10	6.39	0.37	9	8.19	0.18	–	–	–
16 mg S/L Isotherm Parameter (SO4_16) mg S/L												
1	10	11.38	0.24	8	12.42	0.48	9	16.37	0.27	–	–	–
2	8	10.84	0.45	10	11.99	0.19	9	16.20	0.37	–	–	–
4	8	9.75	0.55	10	11.70	0.68	9	15.64	0.19	–	–	–
32 mg S/L Isotherm Parameter (SO4_32) mg S/L												
1	10	23.81	0.93	8	24.35	1.07	9	31.88	0.51	–	–	–
2	8	22.48	1.31	10	25.29	0.46	9	32.56	0.91	–	–	–
4	8	21.07	1.21	10	22.62	2.16	9	31.05	0.40	–	–	–
Total Carbon (C_TOT) wt. %												
1	10	4.57	0.22	8	1.46	0.04	9	0.10	0.01	–	–	–
2	8	4.60	0.20	10	1.44	0.04	9	0.11	0.02	–	–	–
4	8	4.70	0.43	10	1.49	0.03	9	0.10	0.01	6	40.11	0.34
Total Nitrogen (N_TOT) wt. %												
1	10	0.217	0.01	8	0.115	0.00	9	0.005	0.00	–	–	–
2	8	0.220	0.01	10	0.112	0.01	9	0.005	0.00	–	–	–
4	8	0.212	0.01	10	0.116	0.00	9	0.006	0.00	6	1.69	0.03
Total Sulfur (S_TOT) wt. %												
1	10	0.032	0.00	8	0.021	0.00	9	0.002	0.00	–	–	–
2	8	0.032	0.00	10	0.021	0.00	9	0.001	0.00	–	–	–
4	8	0.031	0.00	10	0.021	0.00	9	0.001	0.00	6	0.19	0.01

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[a] Sample size (n), mean, and standard deviation (SD) for B, Bw, C, and O audit samples.

[b] – not analyzed by laboratory.

Appendix G

Range and Frequency Histograms of the Data Sets

This appendix consists of figures displaying histograms of the range and frequency distribution of the routine samples (RS), the field duplicates (FD), the preparation duplicates (PD), and the laboratory audit samples (AS). Supplemental information relating to these plots can be found under "Representativeness" in Sections 2 and 3 of the report. Histograms are presented for each of the 50 analytical parameters in the order described in Table 1-1 of Section 1 of the report.

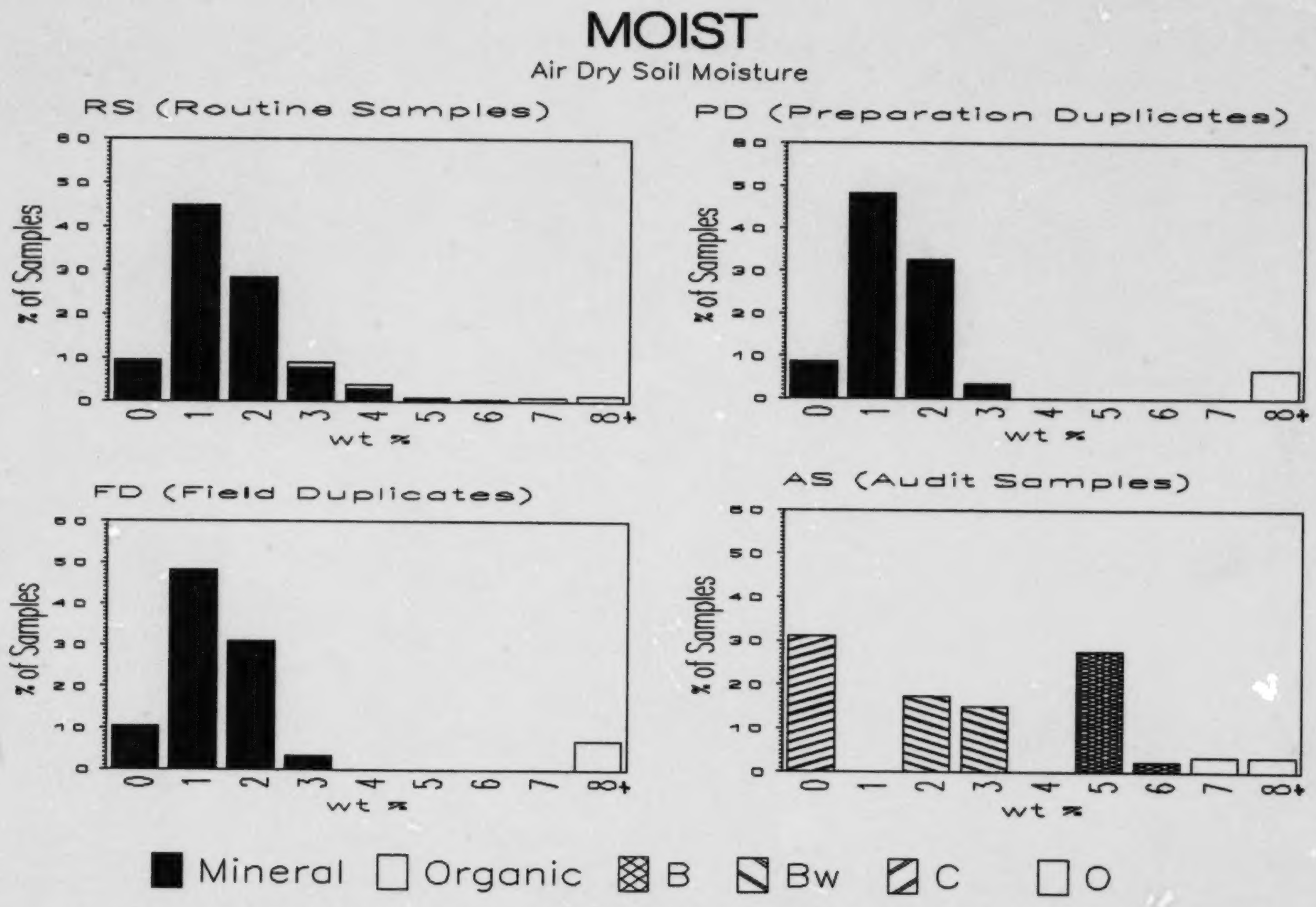


Figure G-1. Range and frequency distribution for MOIST.

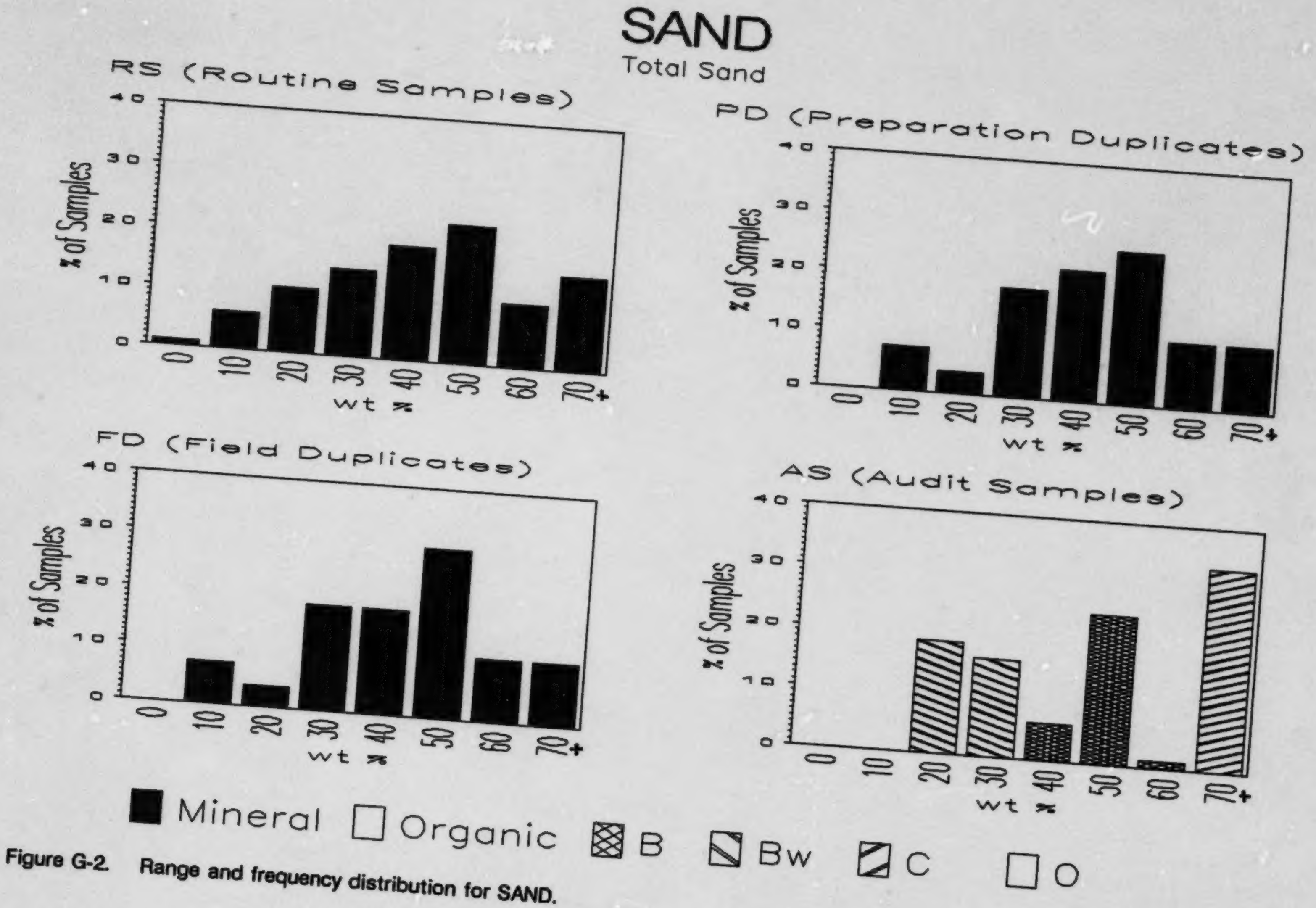


Figure G-2. Range and frequency distribution for SAND.

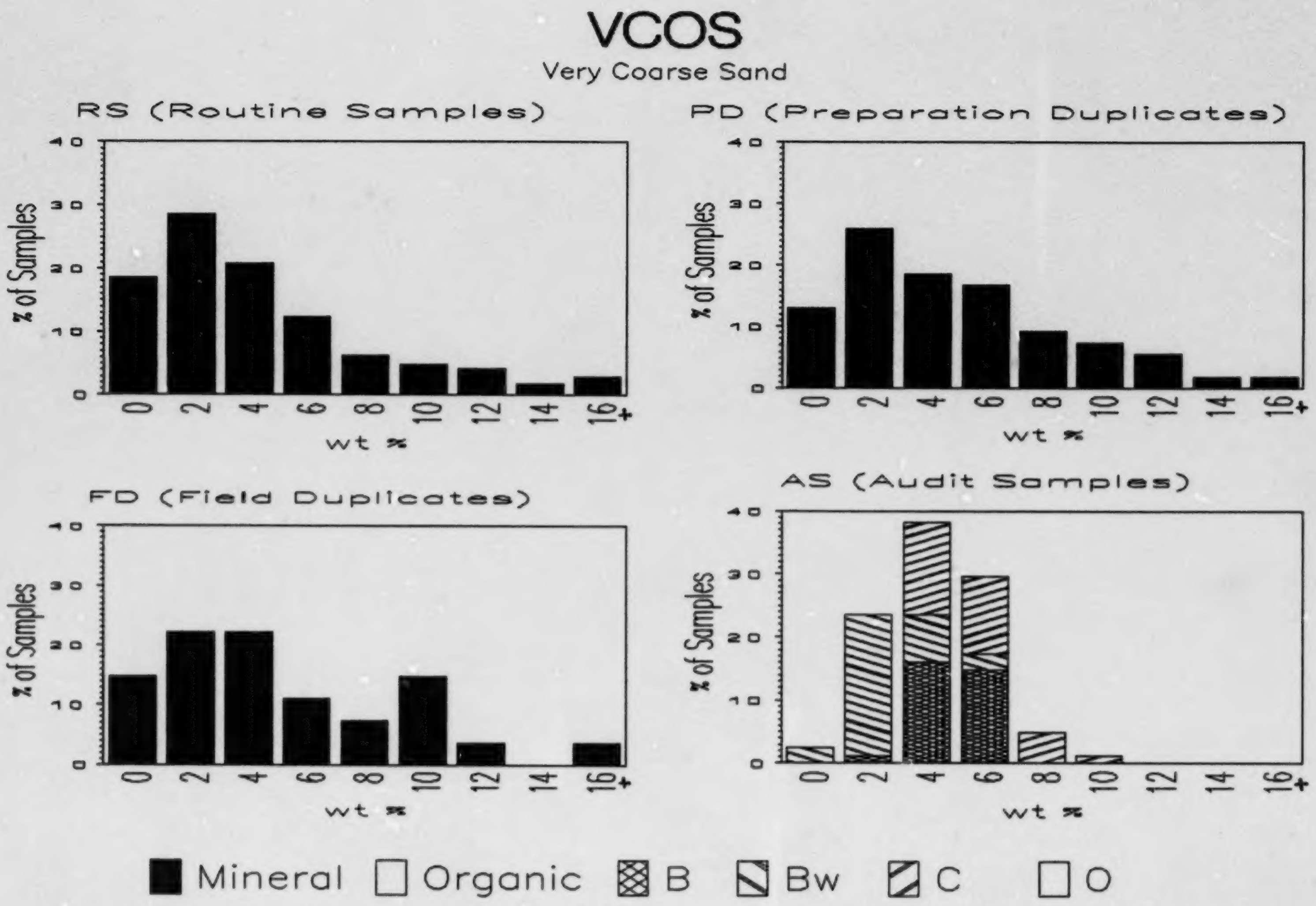


Figure G-3. Range and frequency distribution for VCOS.

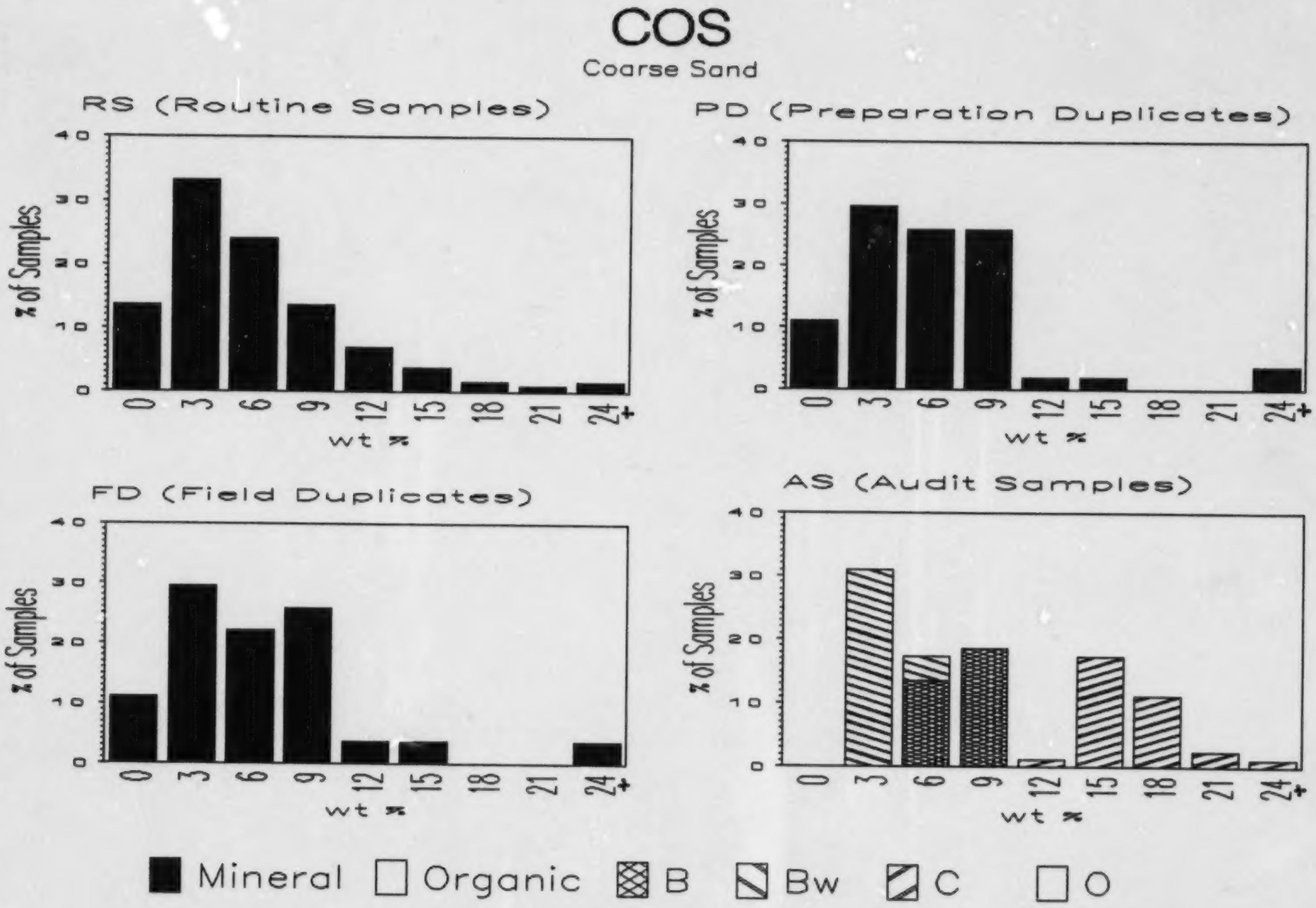


Figure G-4. Range and frequency distribution for COS.

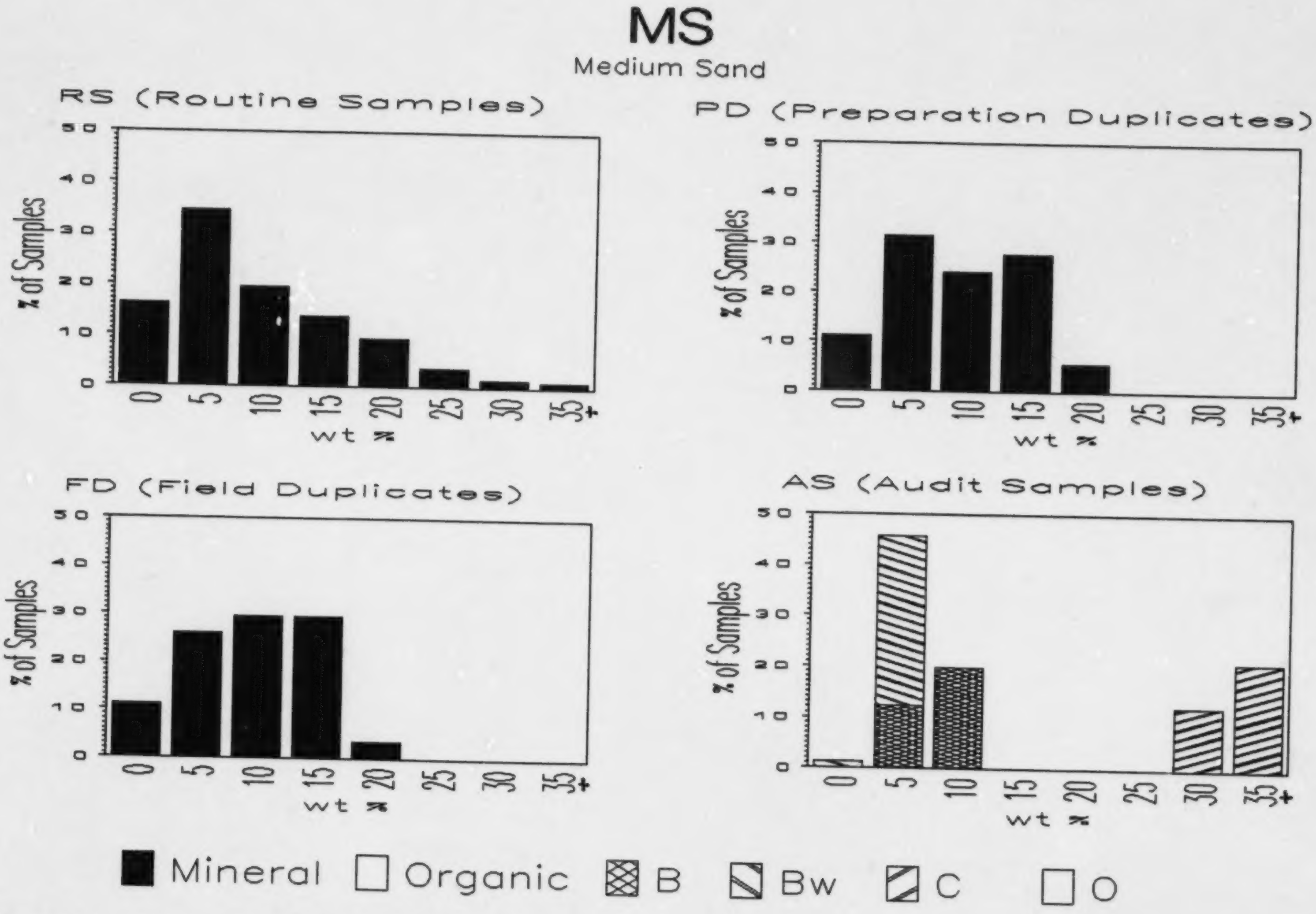


Figure G-5. Range and frequency distribution for MS.

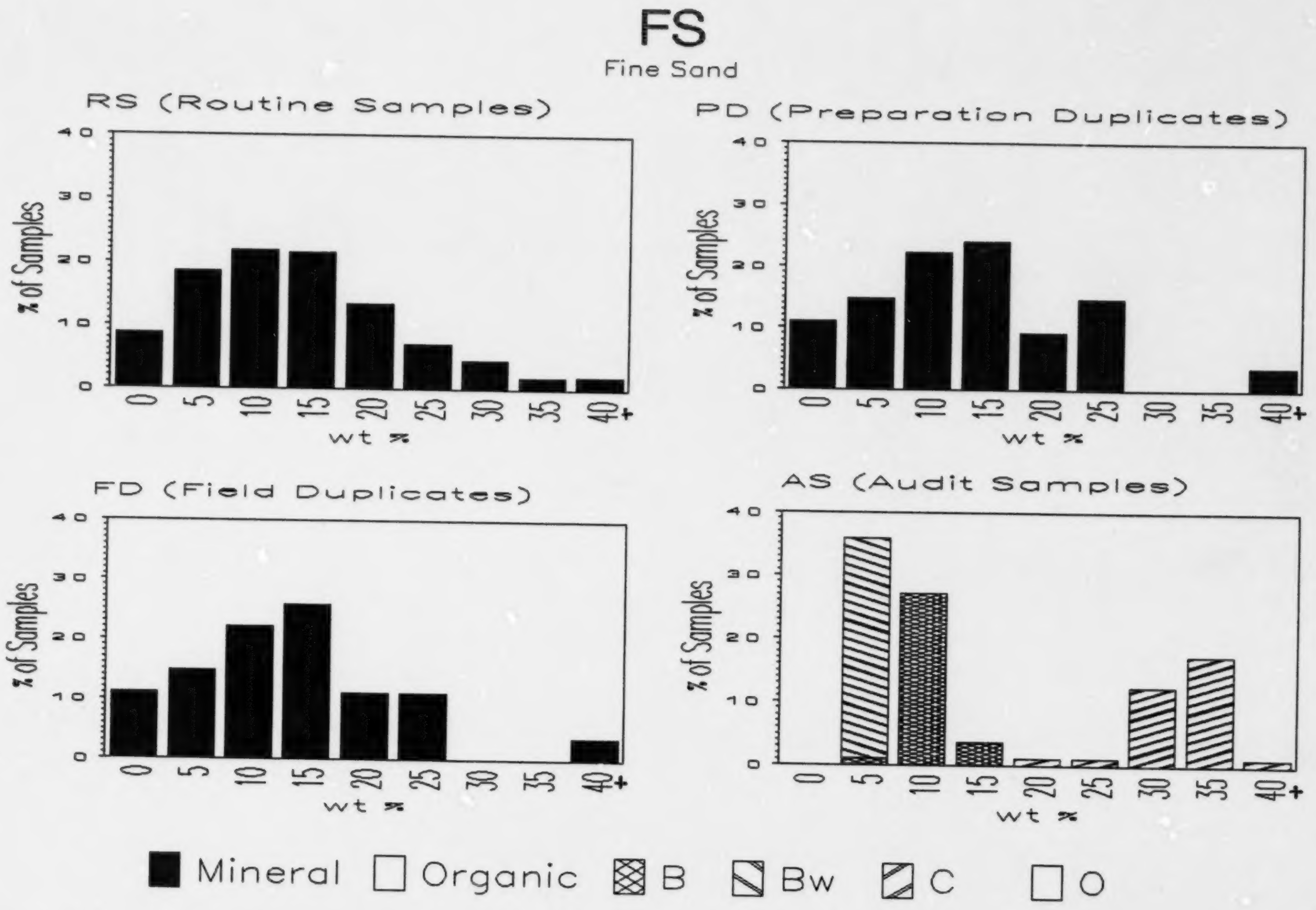


Figure G-6. Range and frequency distribution for FS.

5

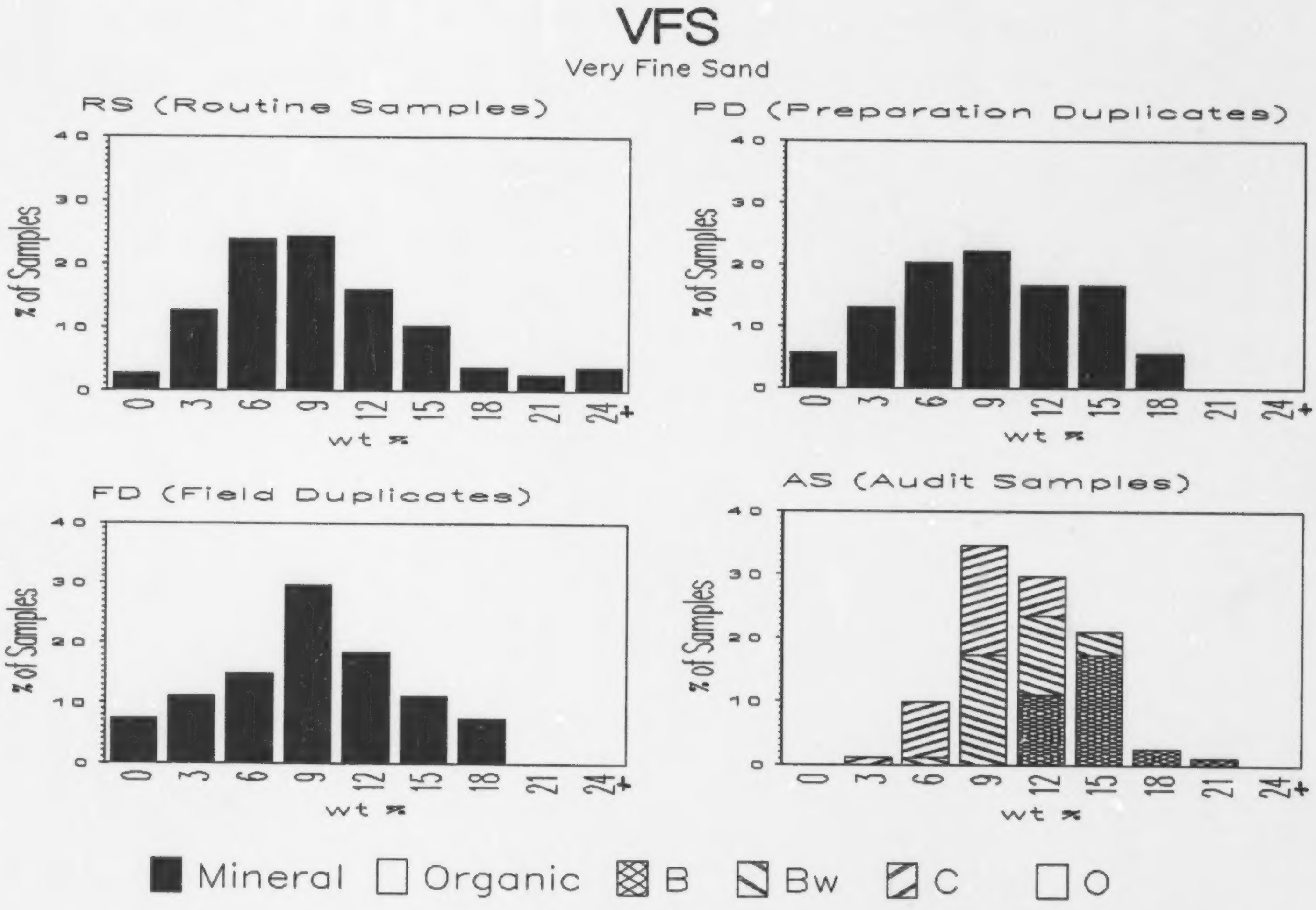


Figure G-7. Range and frequency distribution for VFS.

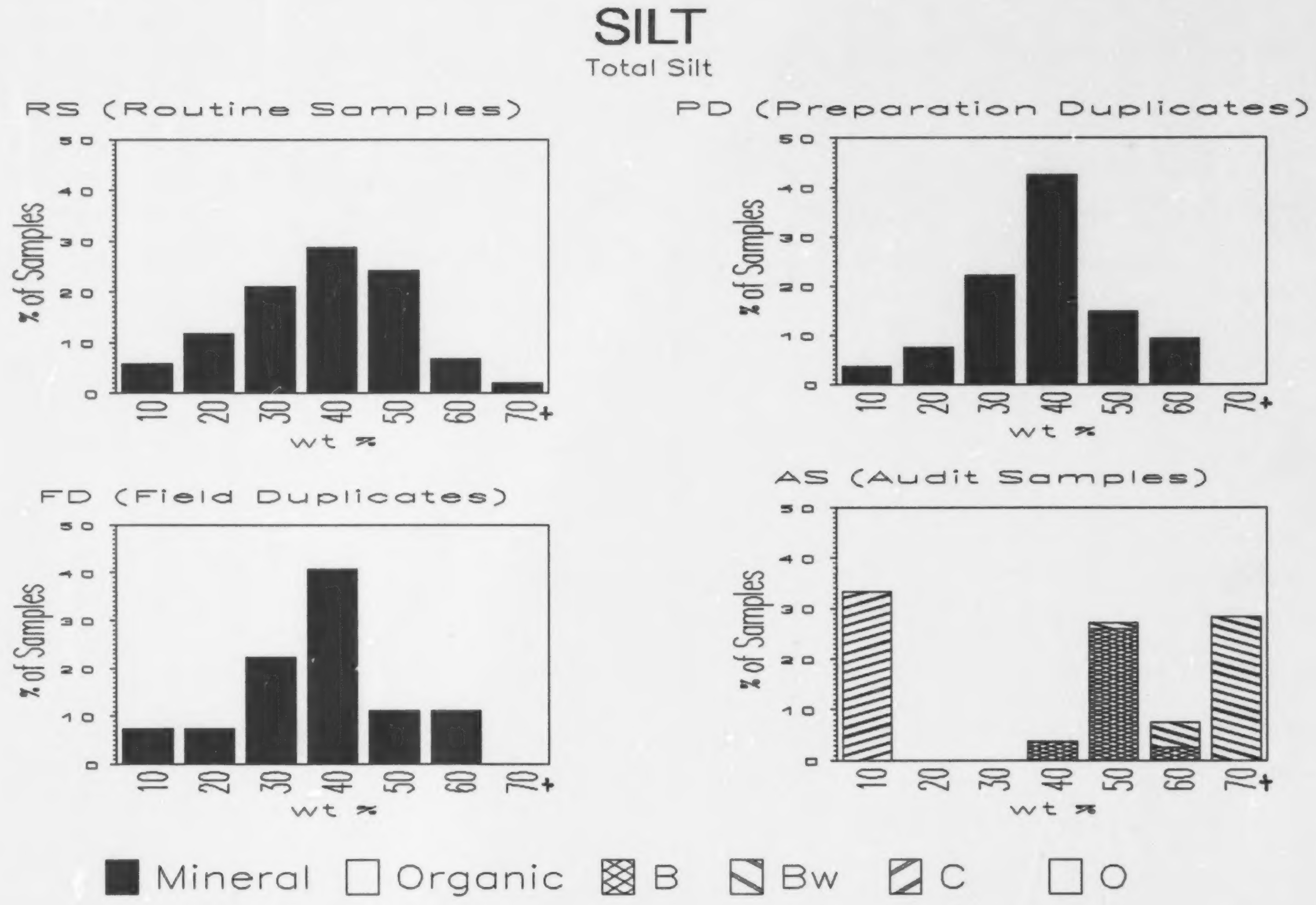


Figure G-8. Range and frequency distribution for SILT.

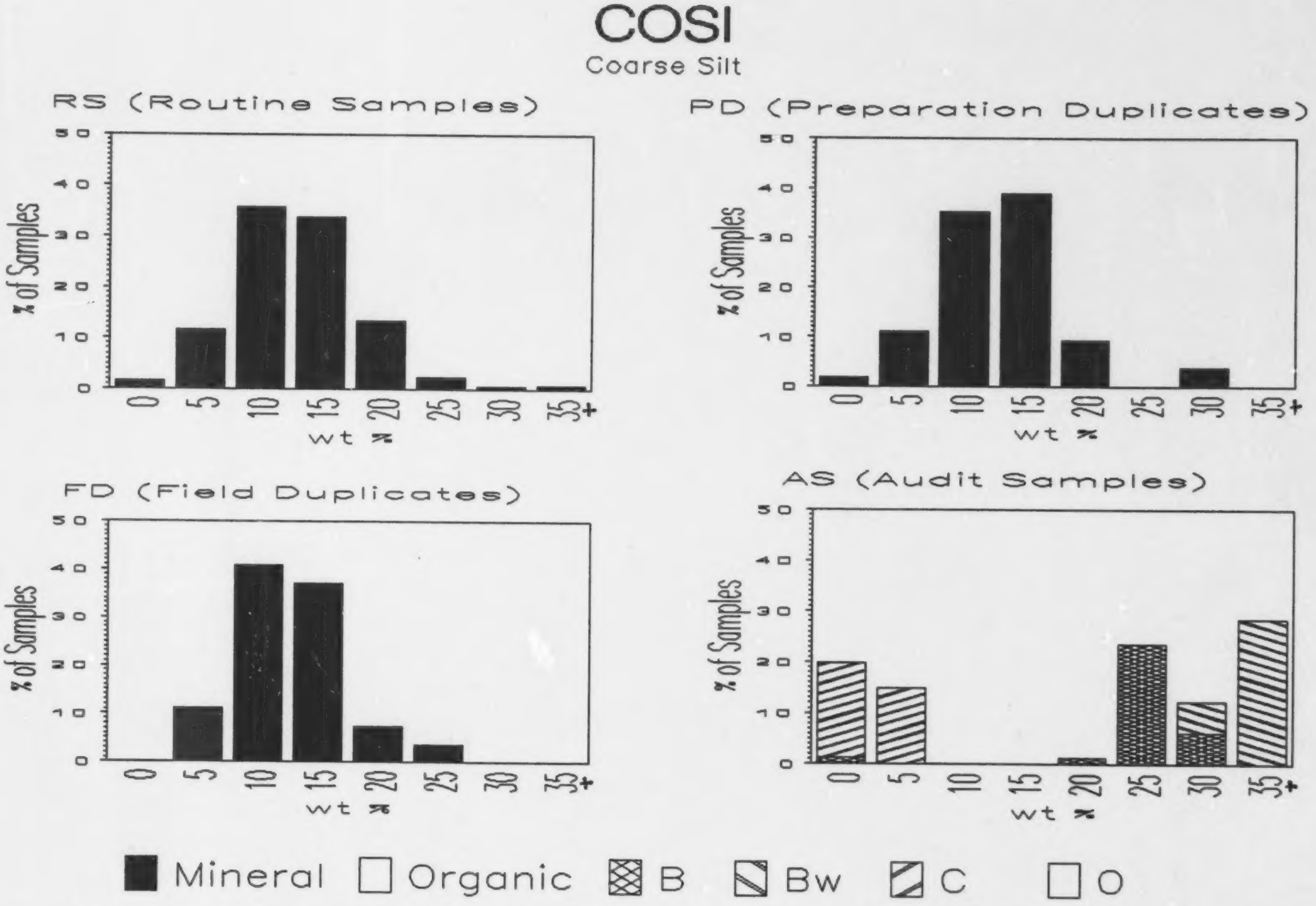


Figure G-9. Range and frequency distribution for COSI.

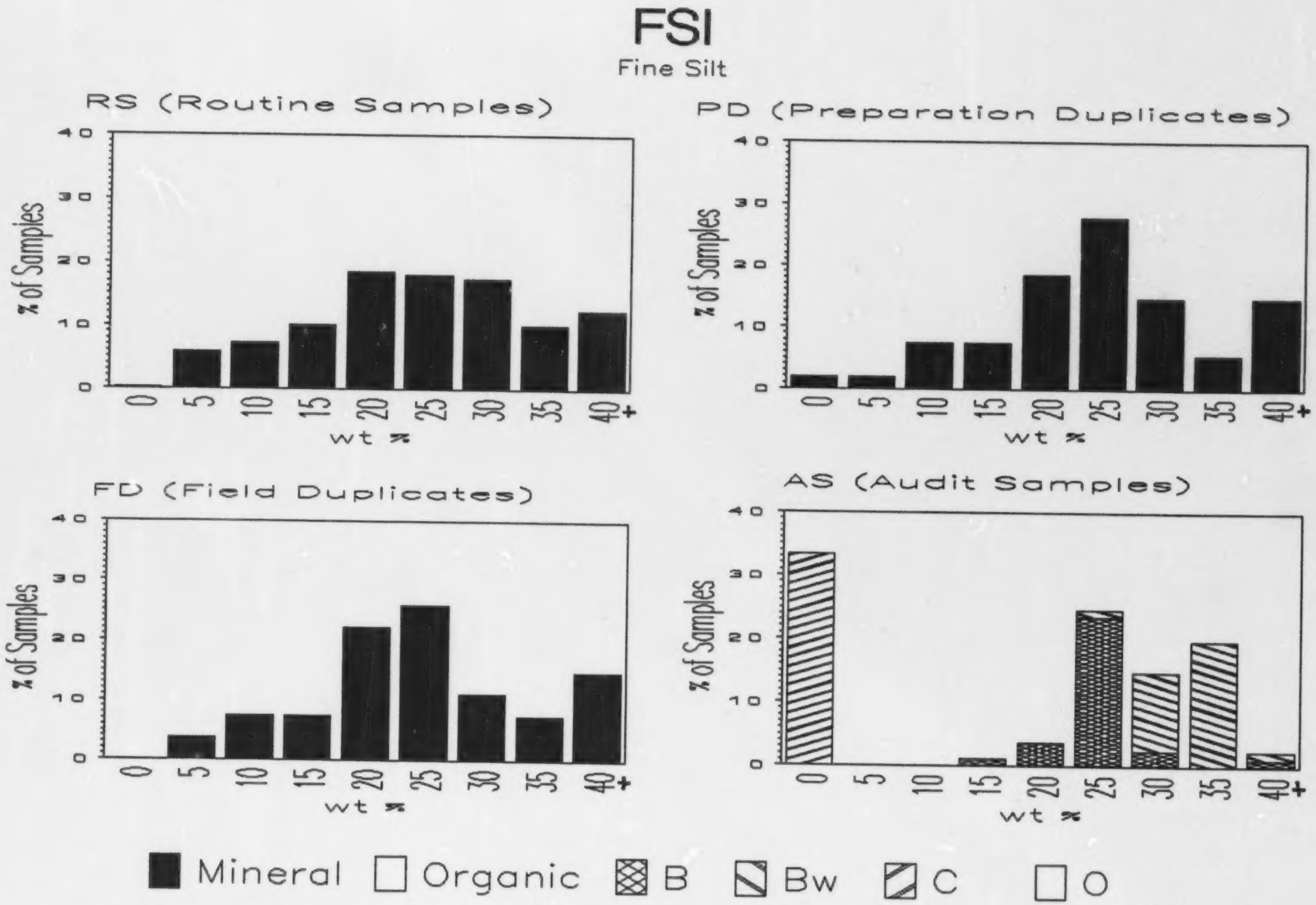


Figure G-10. Range and frequency distribution for FSI.

CLAY

Total Clay

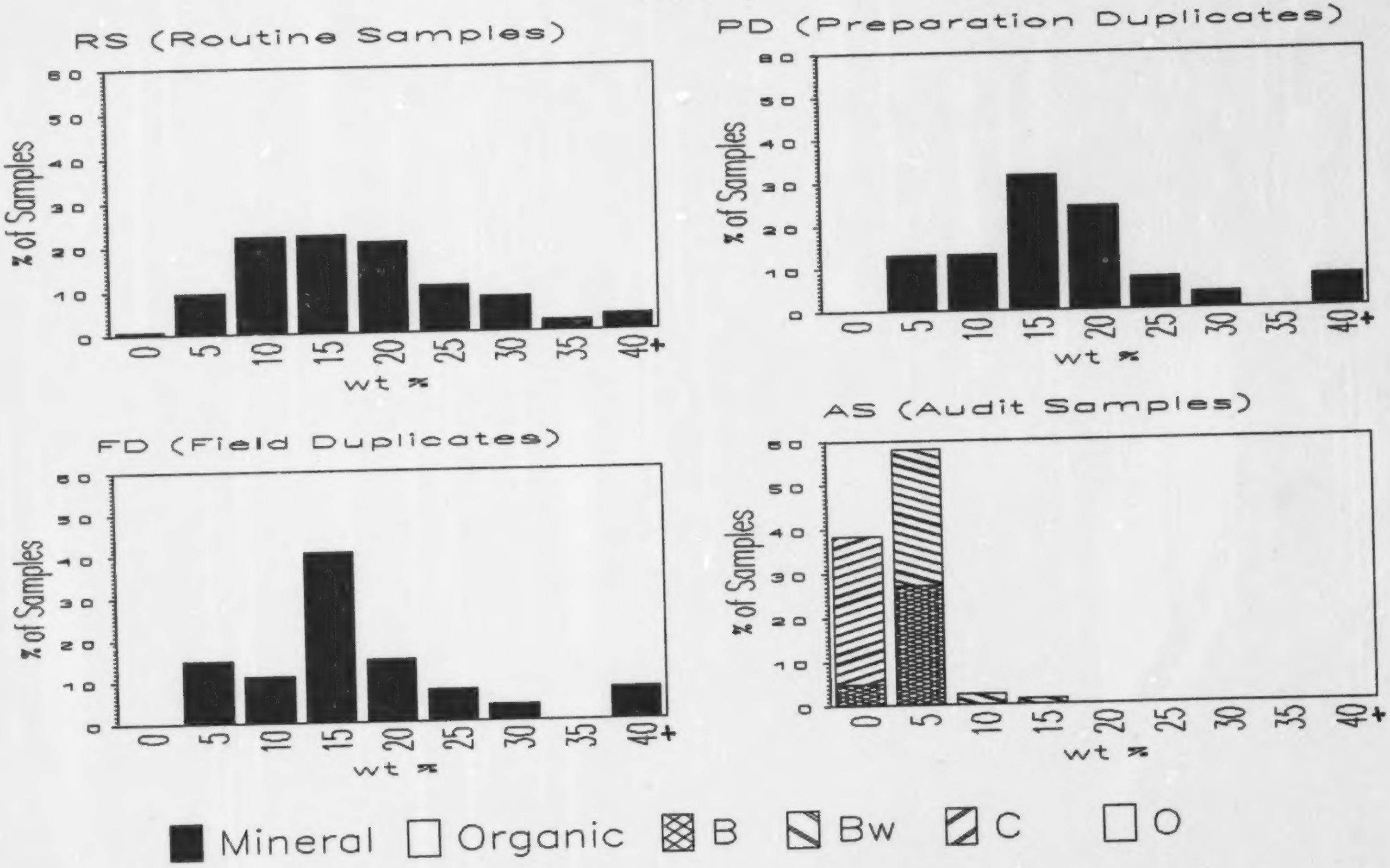


Figure G-11. Range and frequency distribution for CLAY.

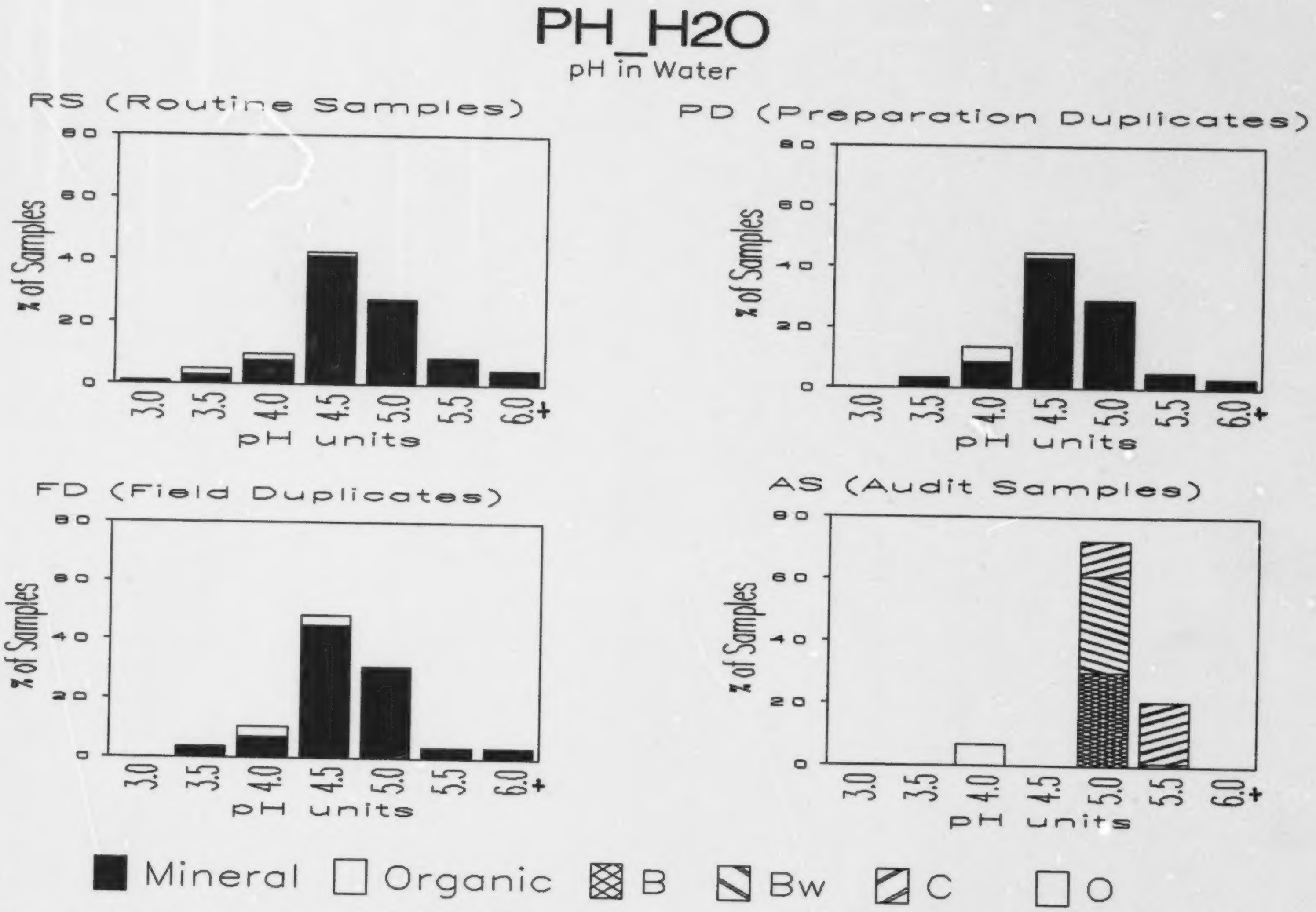


Figure G-12. Range and frequency distribution for PH_H20.

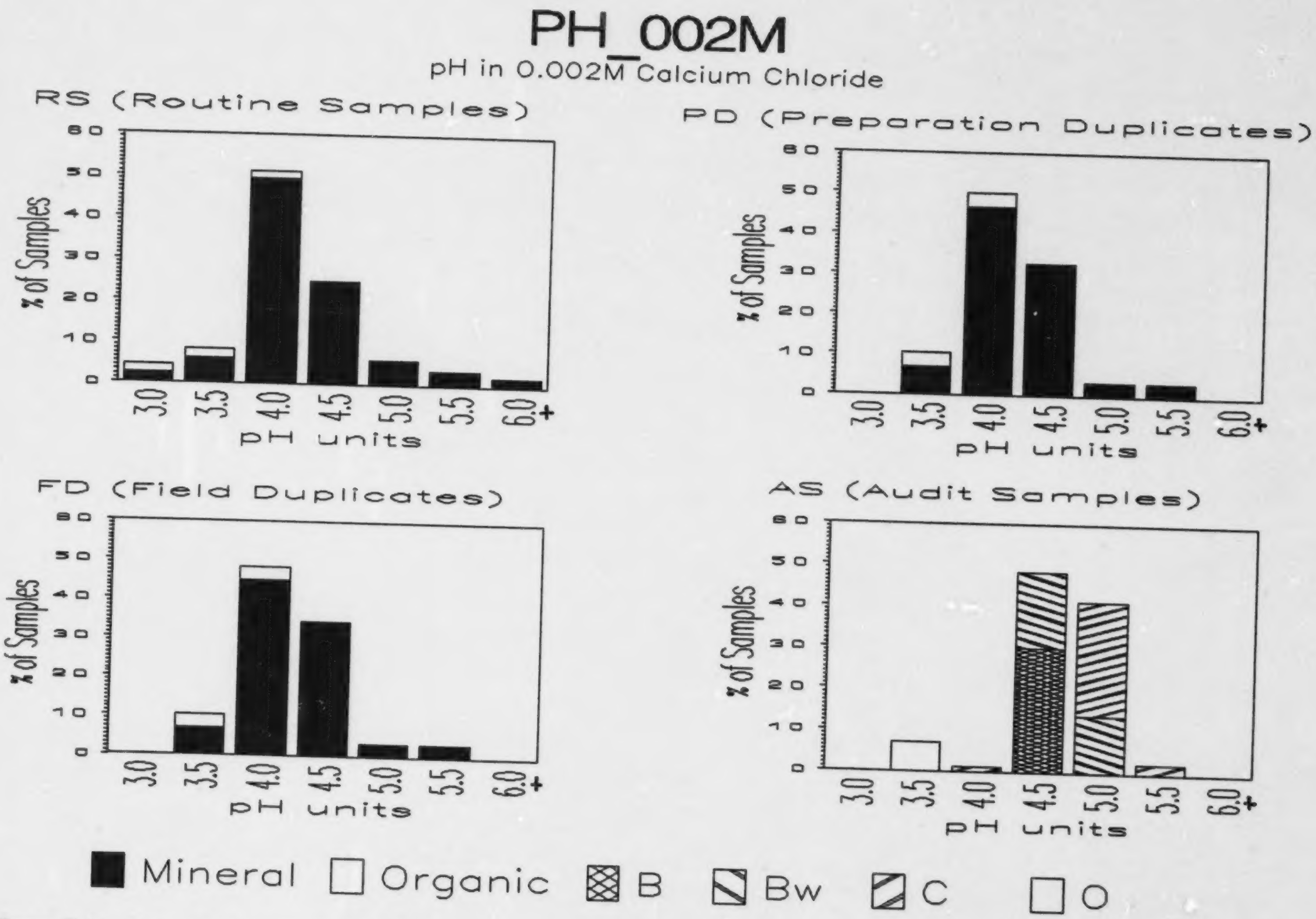


Figure G-13. Range and frequency distribution for PH_002M.

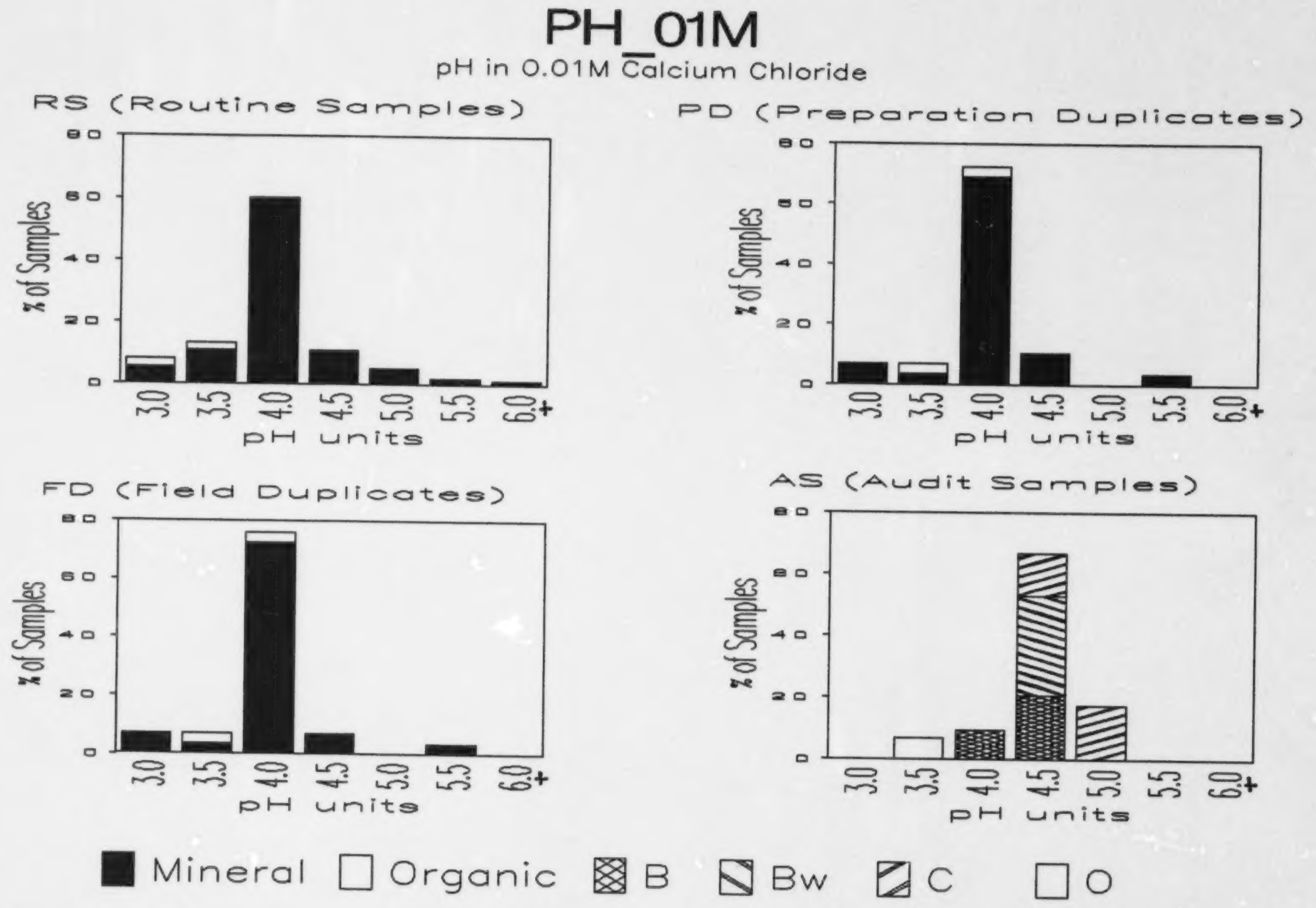


Figure G-14. Range and frequency distribution for PH_01M.

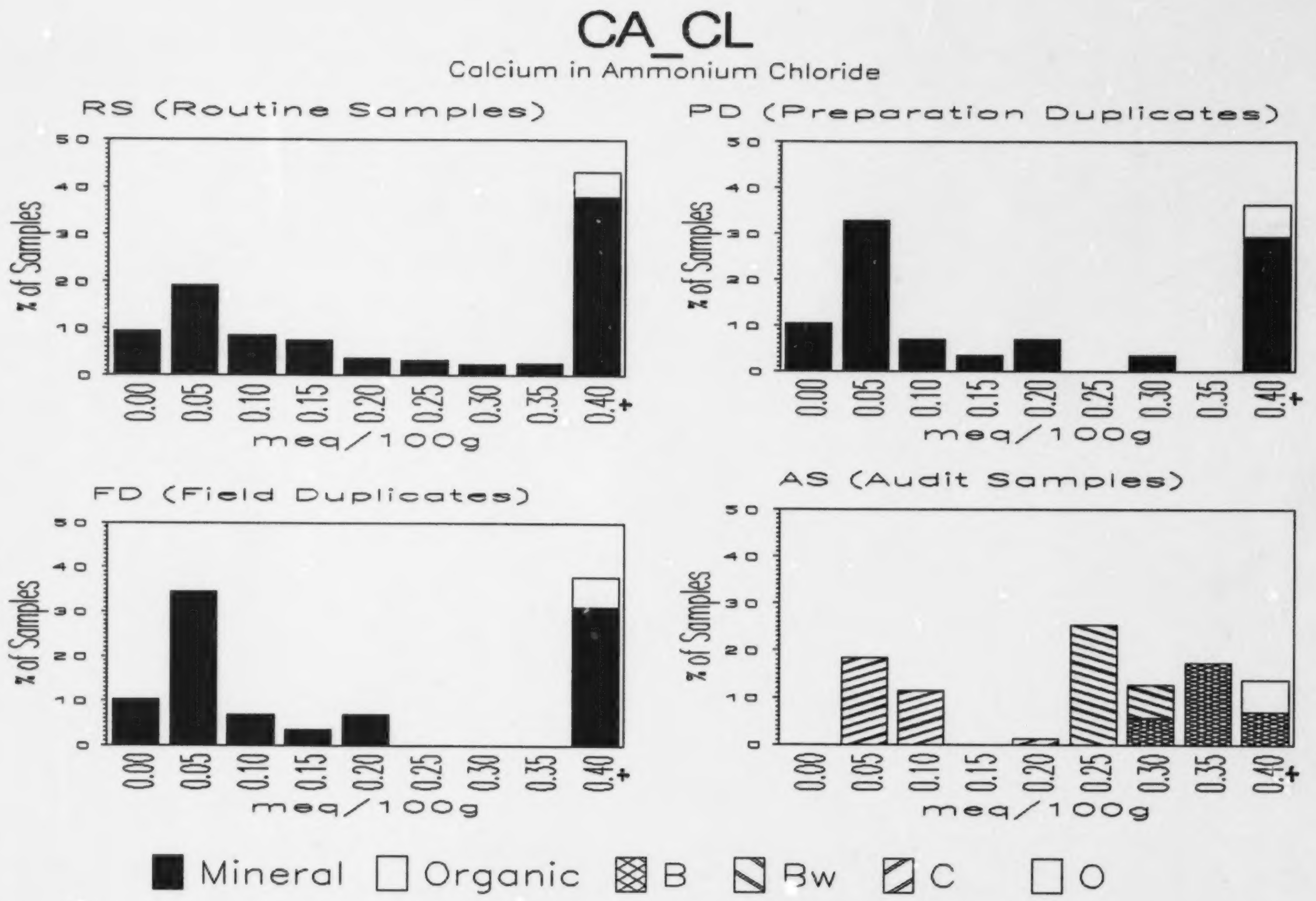


Figure G-15. Range and frequency distribution for CA_CL.

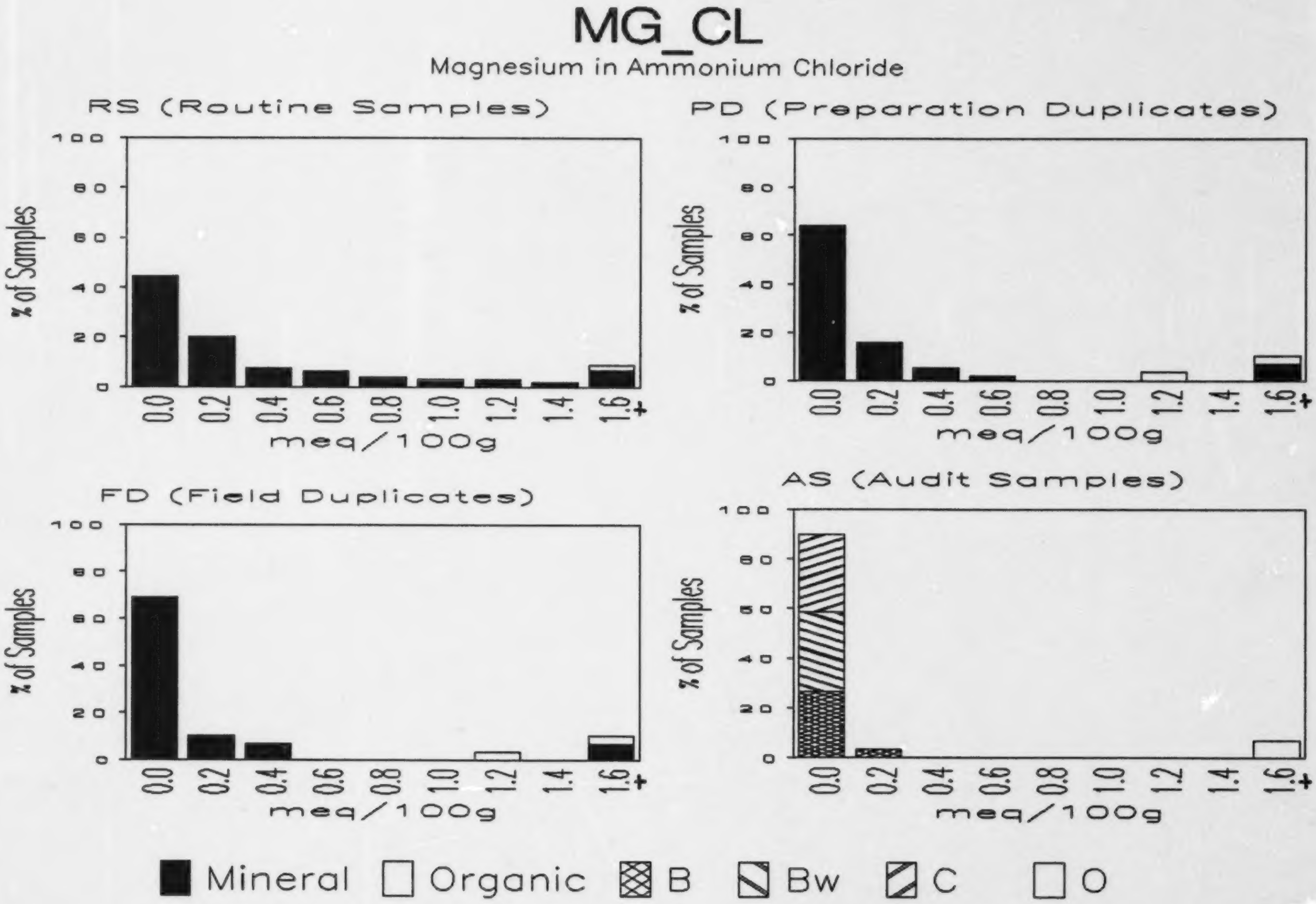


Figure G-16. Range and frequency distribution for MG_CL.

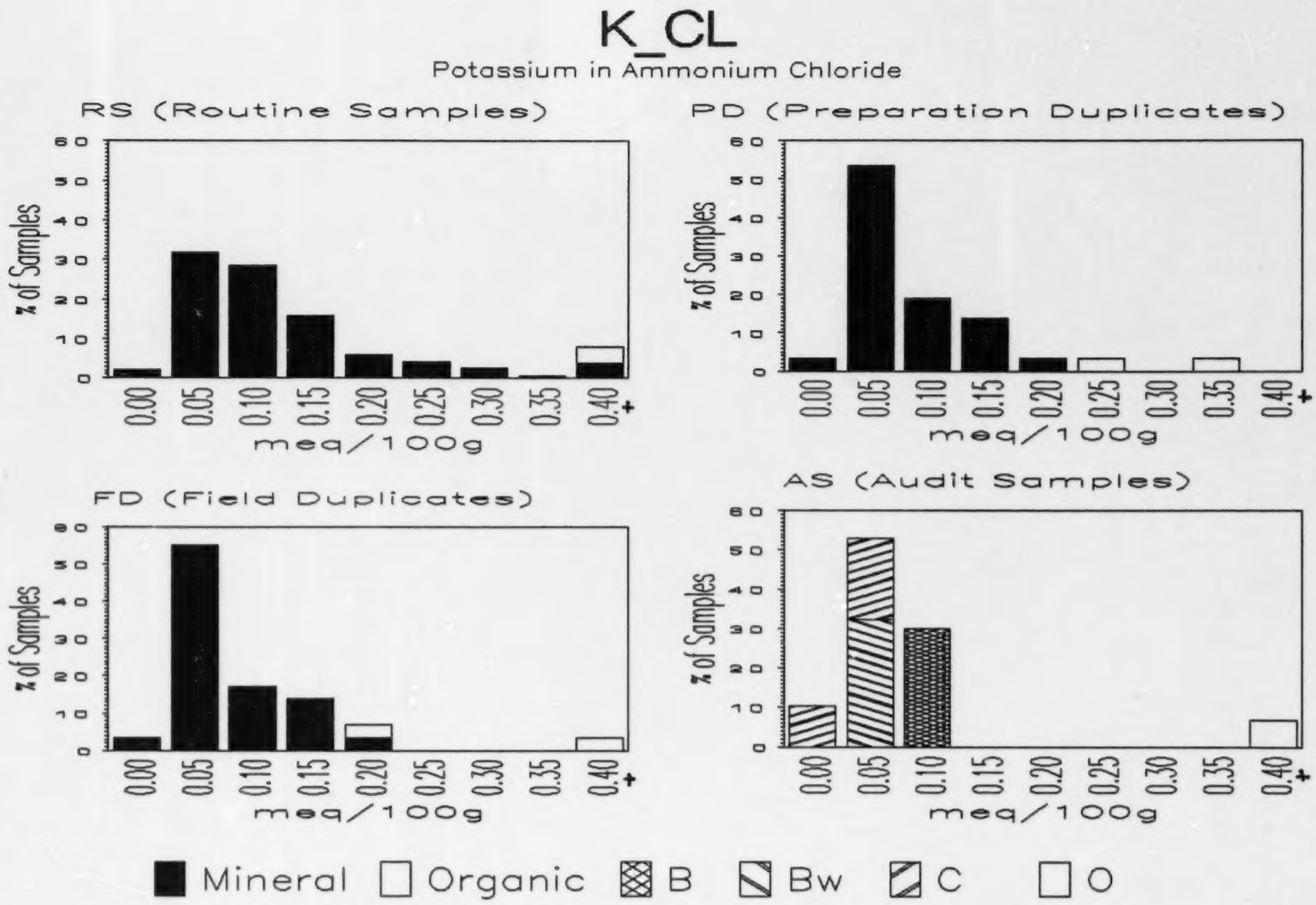


Figure G-17. Range and frequency distribution for K_CL.

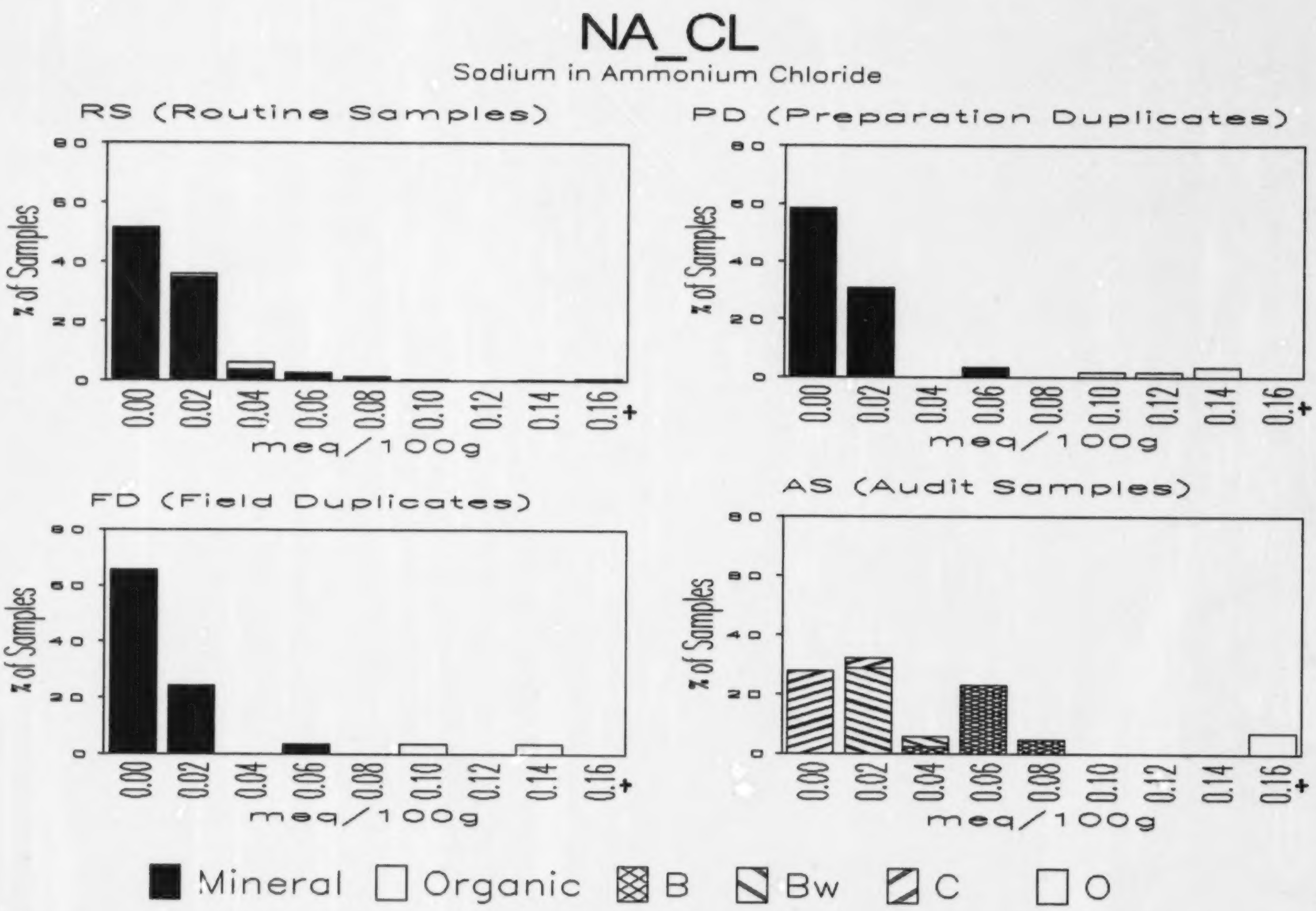


Figure G-18. Range and frequency distribution for NA_CL.

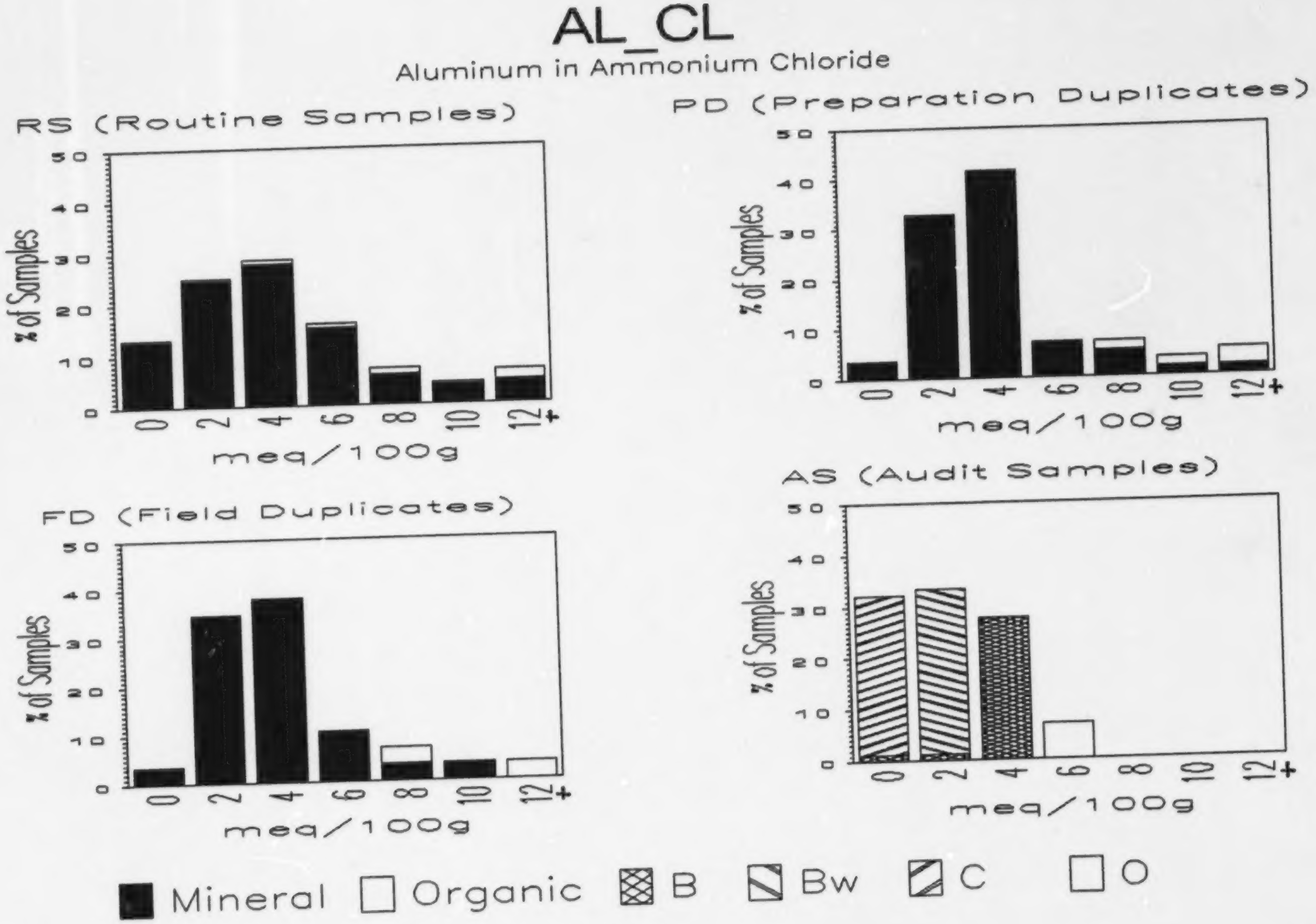


Figure G-19. Range and frequency distribution for AL_CL.

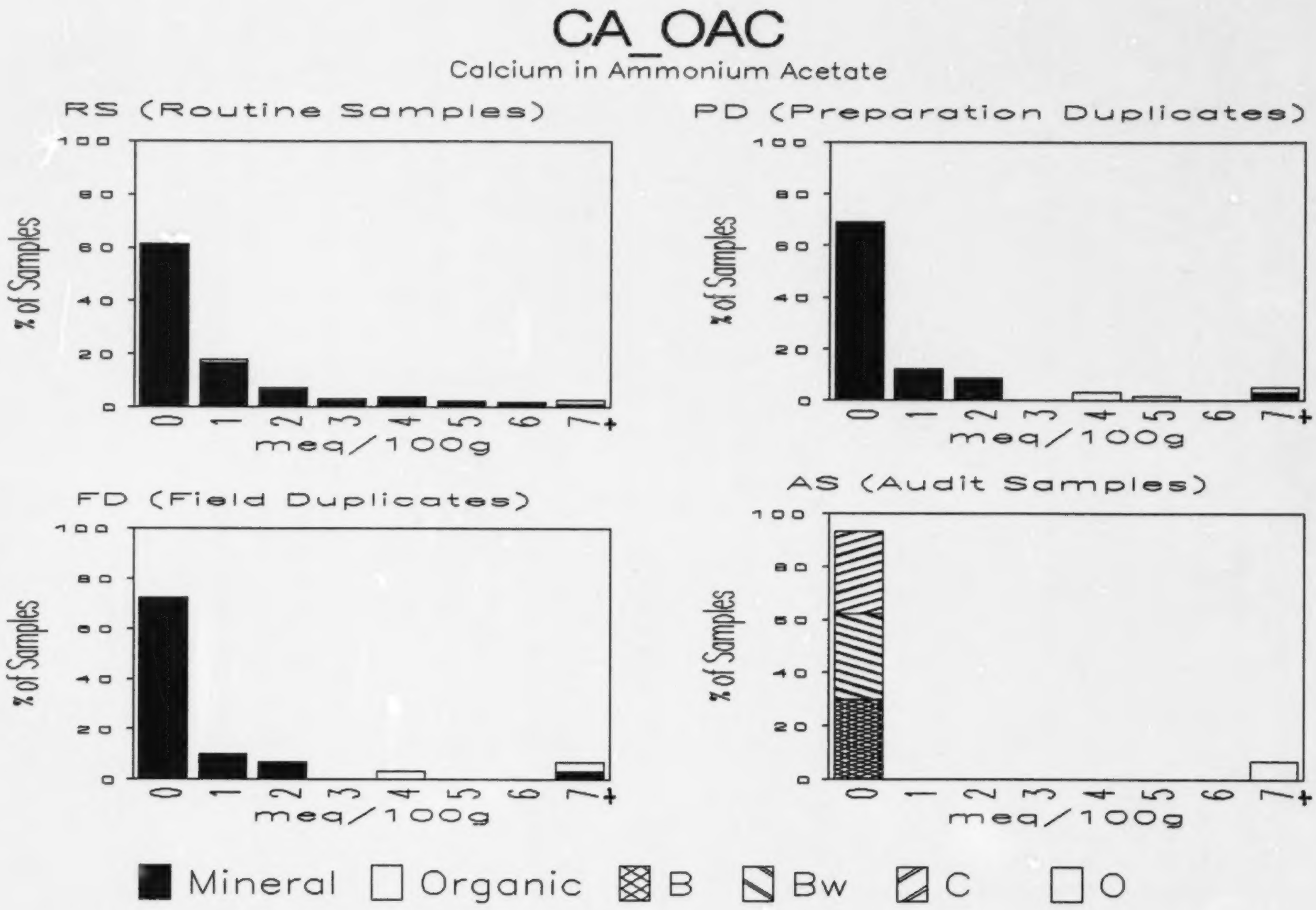


Figure G-20. Range and frequency distribution for CA_OAC.

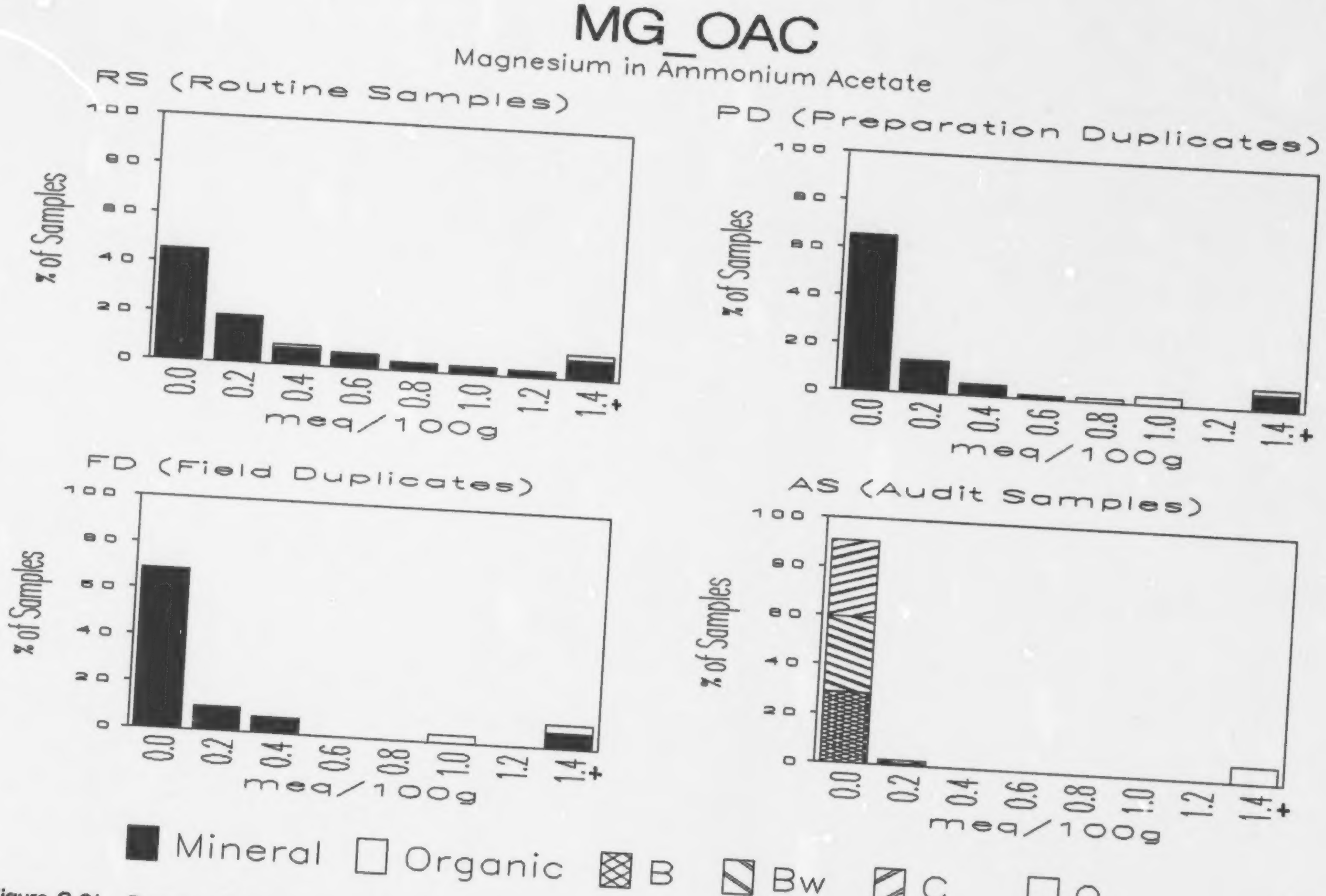


Figure G-21. Range and frequency distribution for MG_OAC.

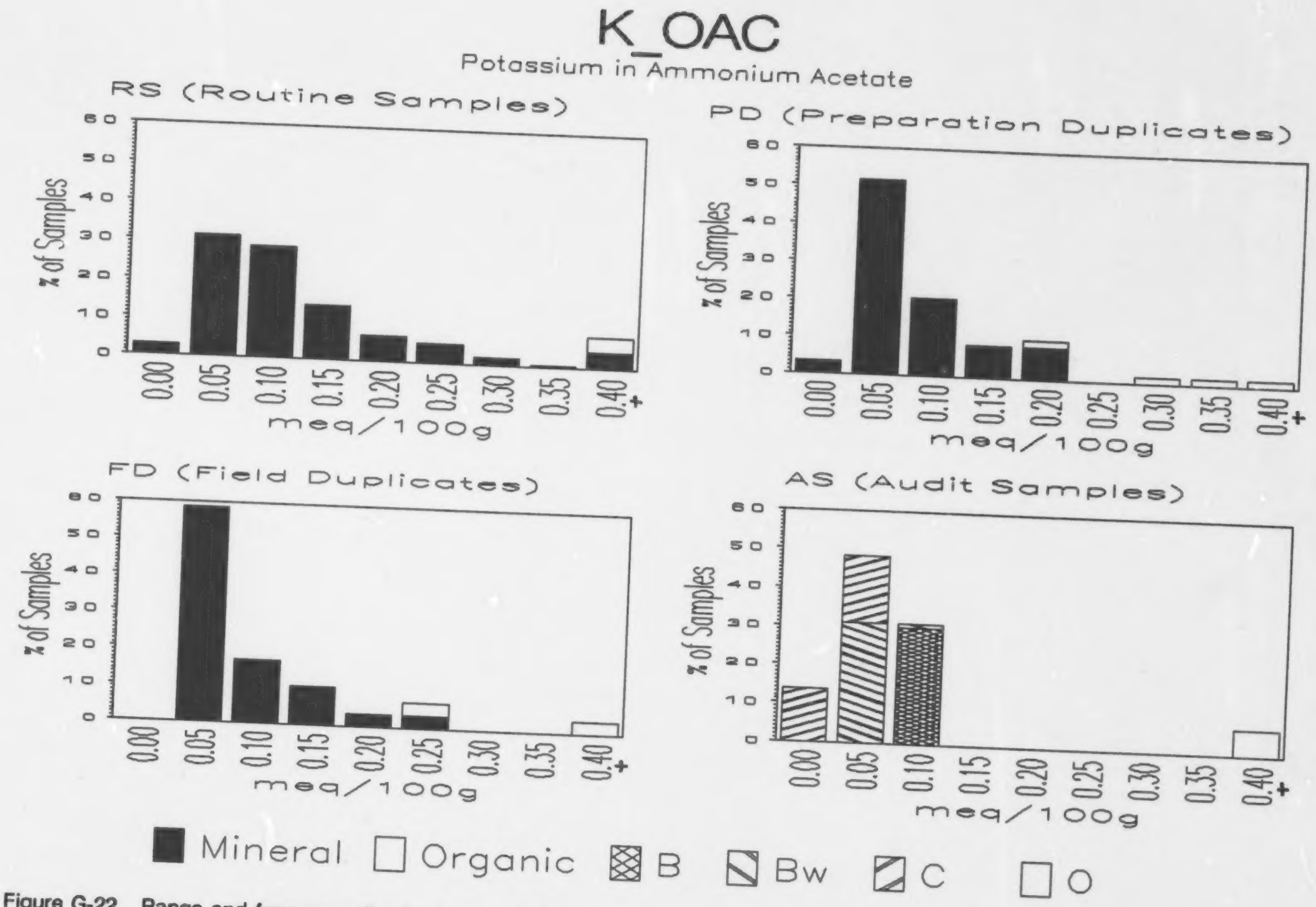


Figure G-22. Range and frequency distribution for K_OAC.

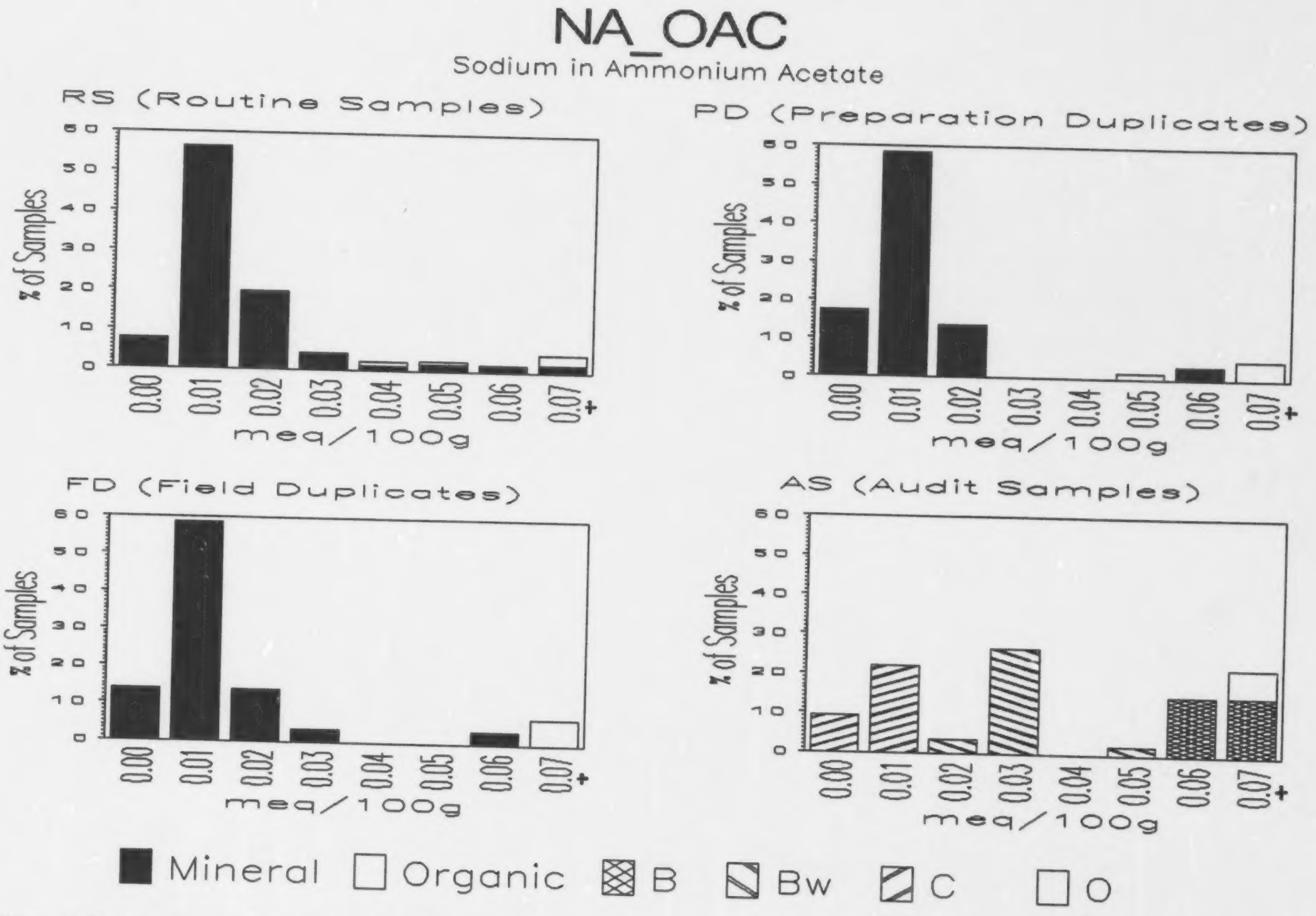


Figure G-23. Range and frequency distribution for NA_OAC.

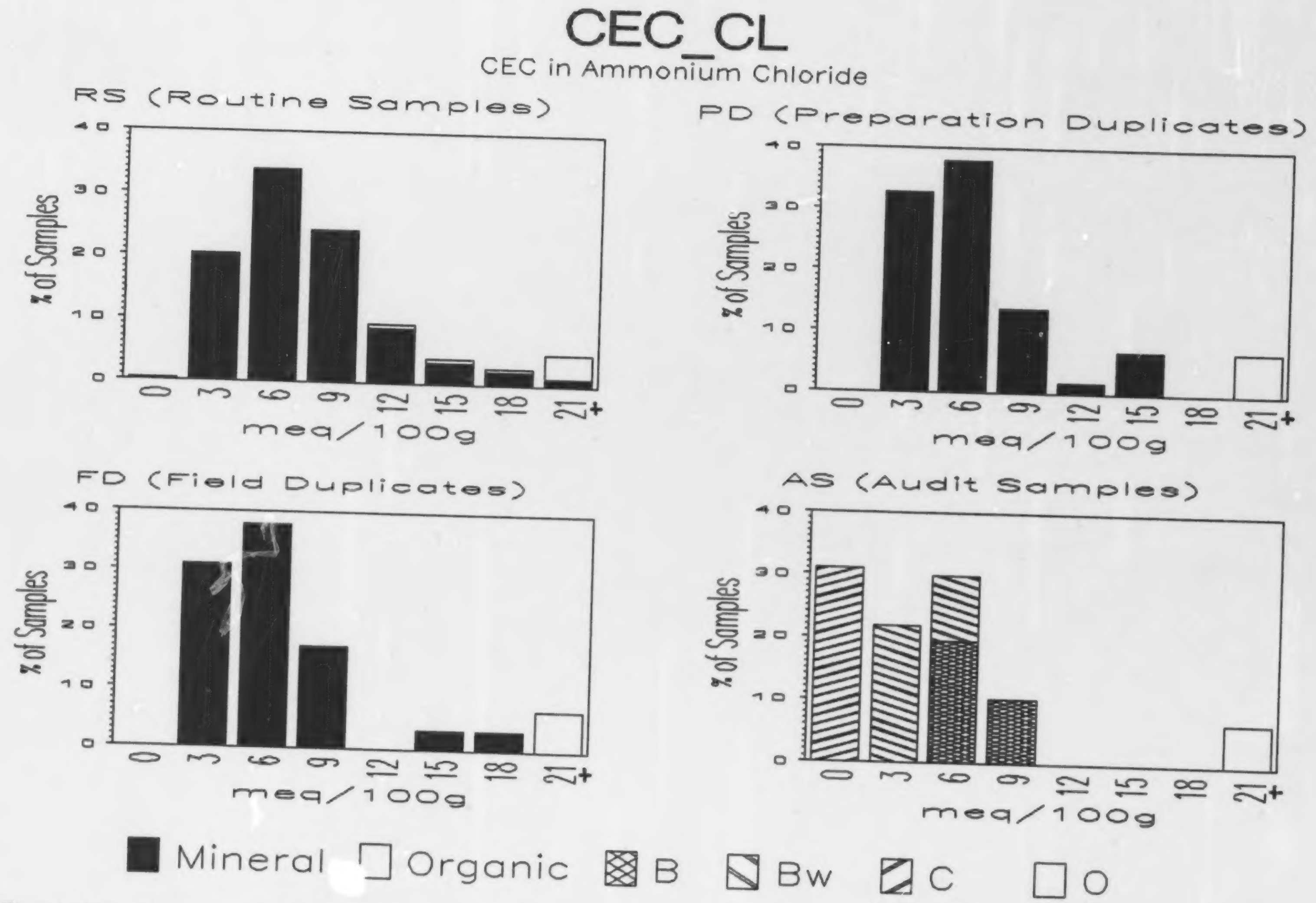


Figure G-24. Range and frequency distribution for CEC_CL.

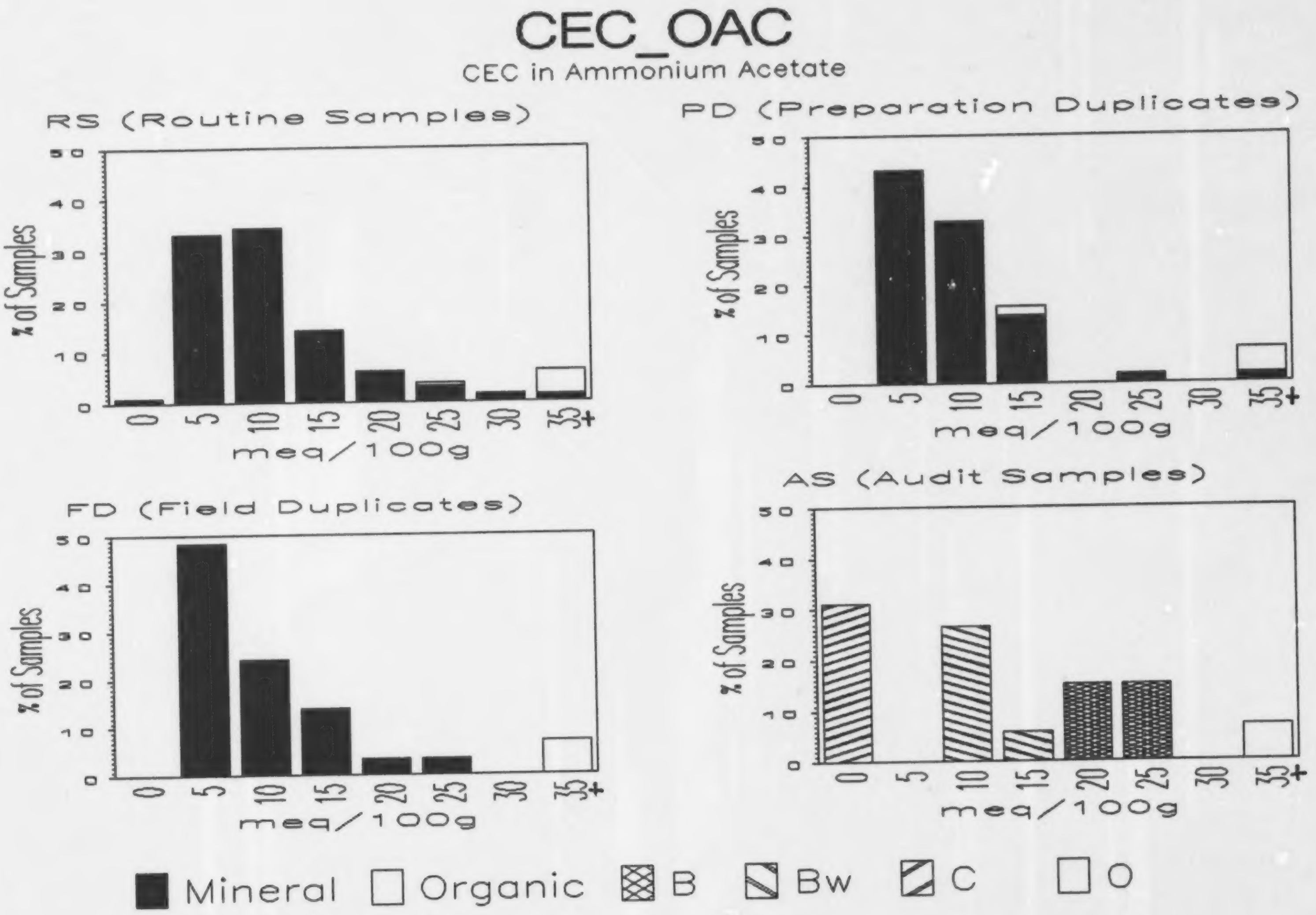


Figure G-25. Range and frequency distribution for CEC_OAC.

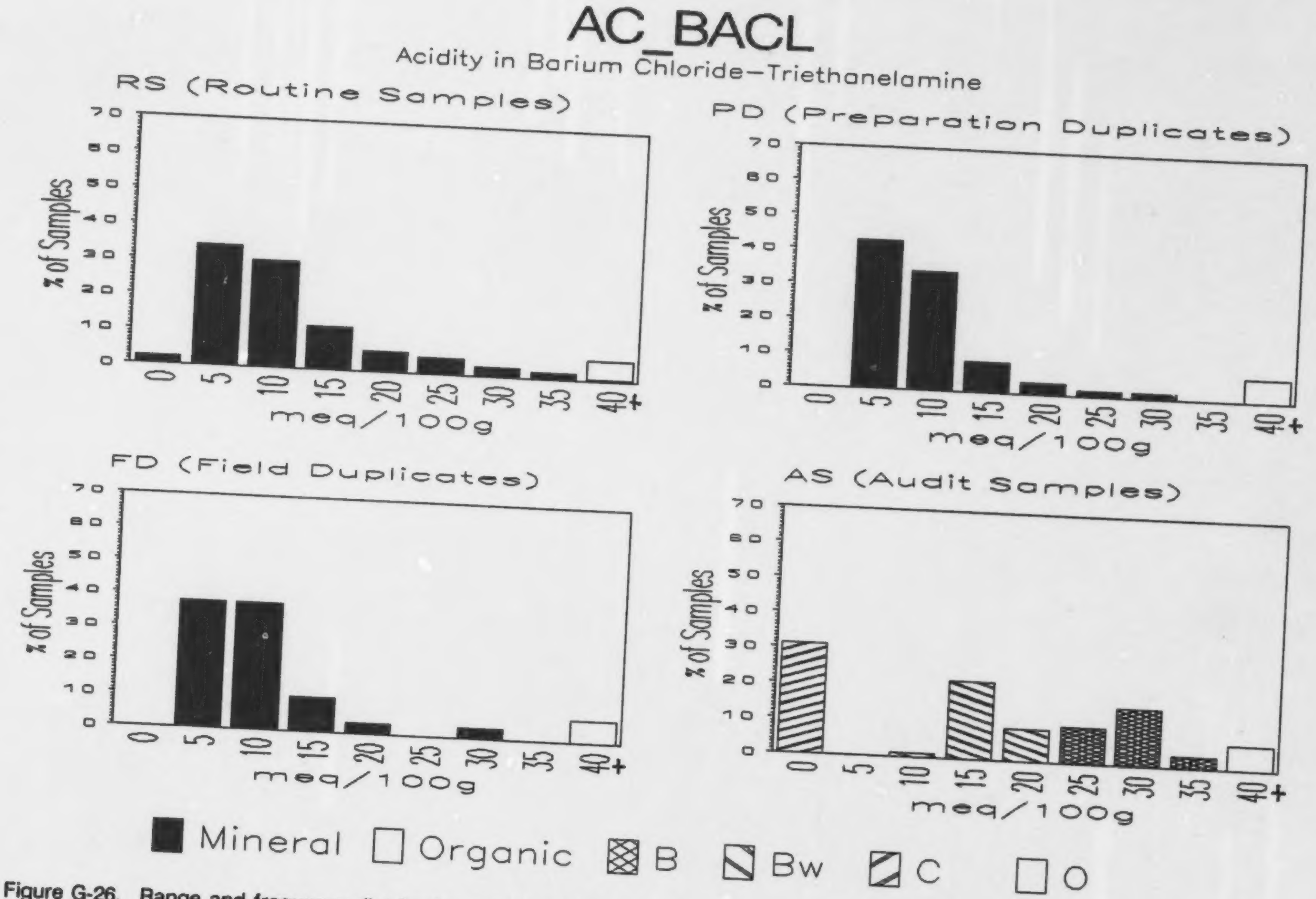


Figure G-26. Range and frequency distribution for AC_BACL.

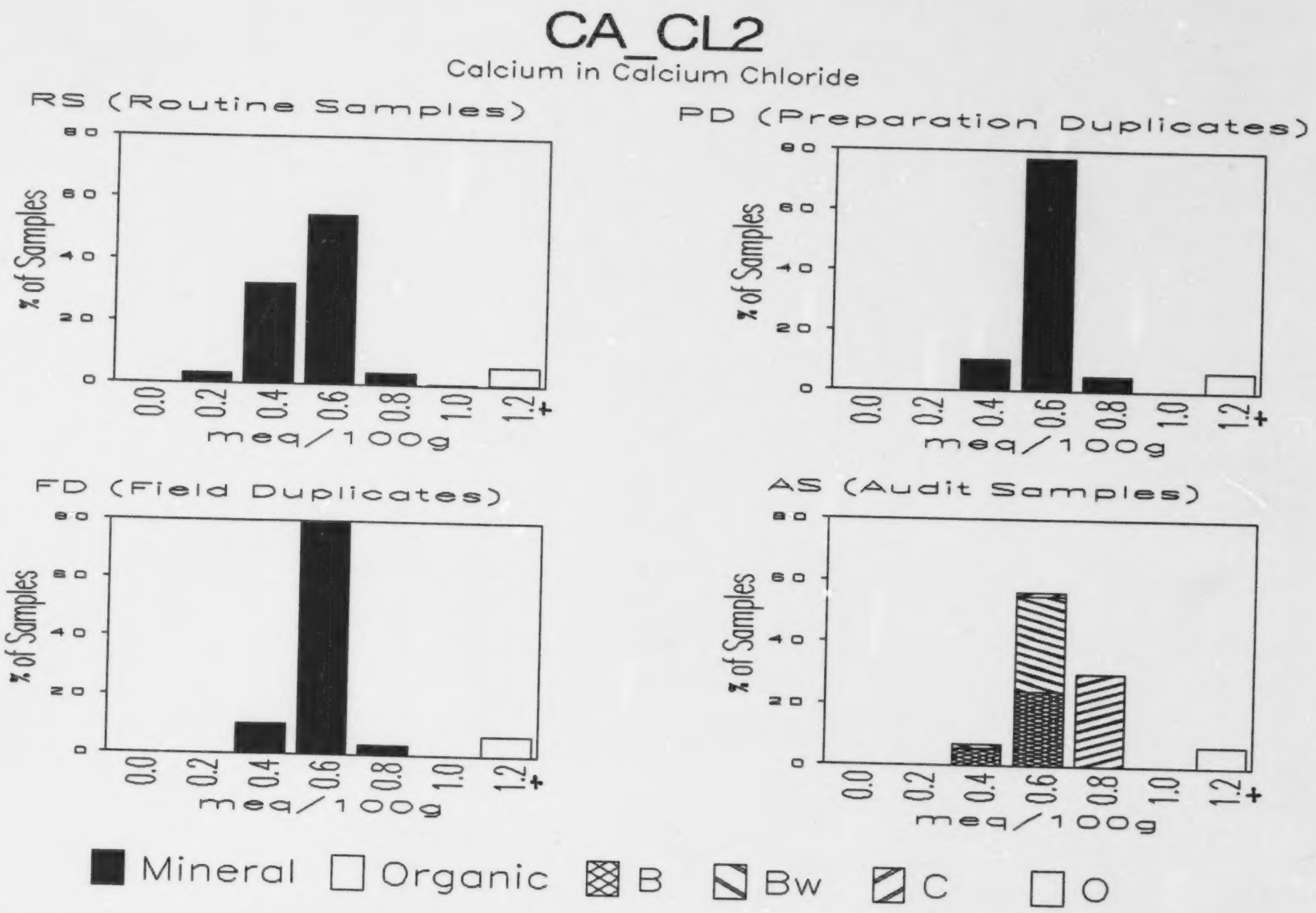


Figure G-27. Range and frequency distribution for CA_CL2.

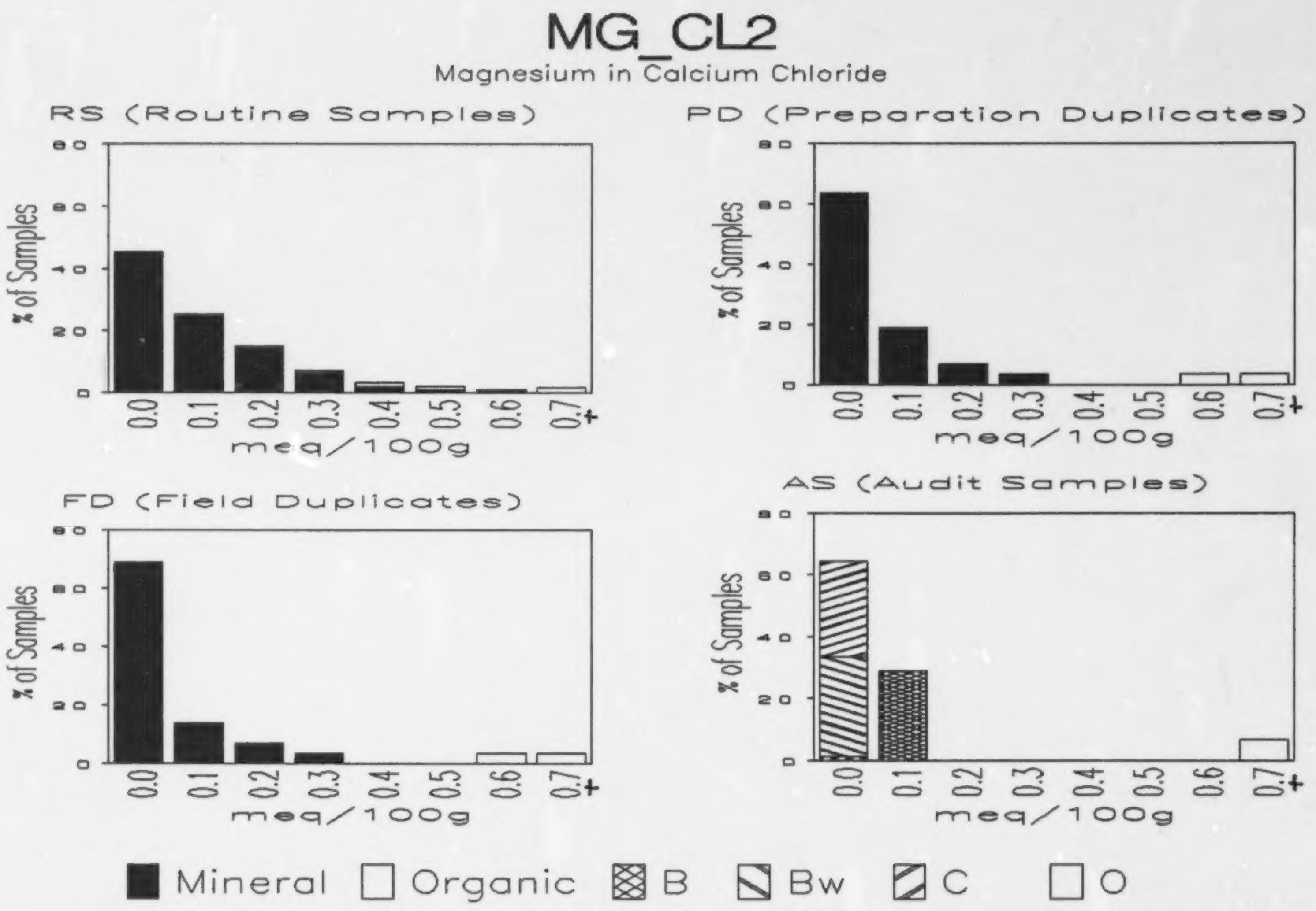


Figure G-28. Range and frequency distribution for MG_CL2.

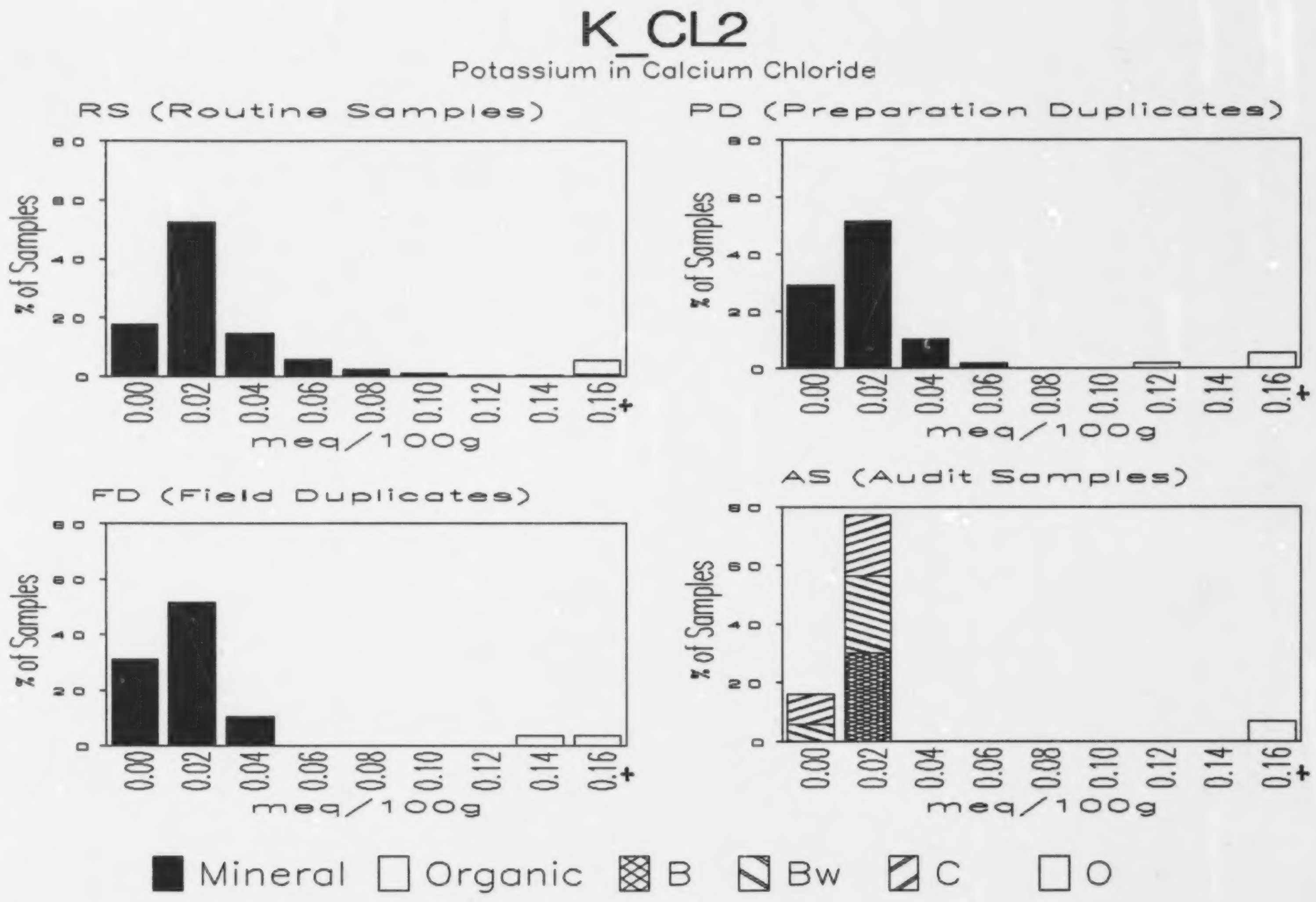


Figure G-29. Range and frequency distribution for K_CL2.

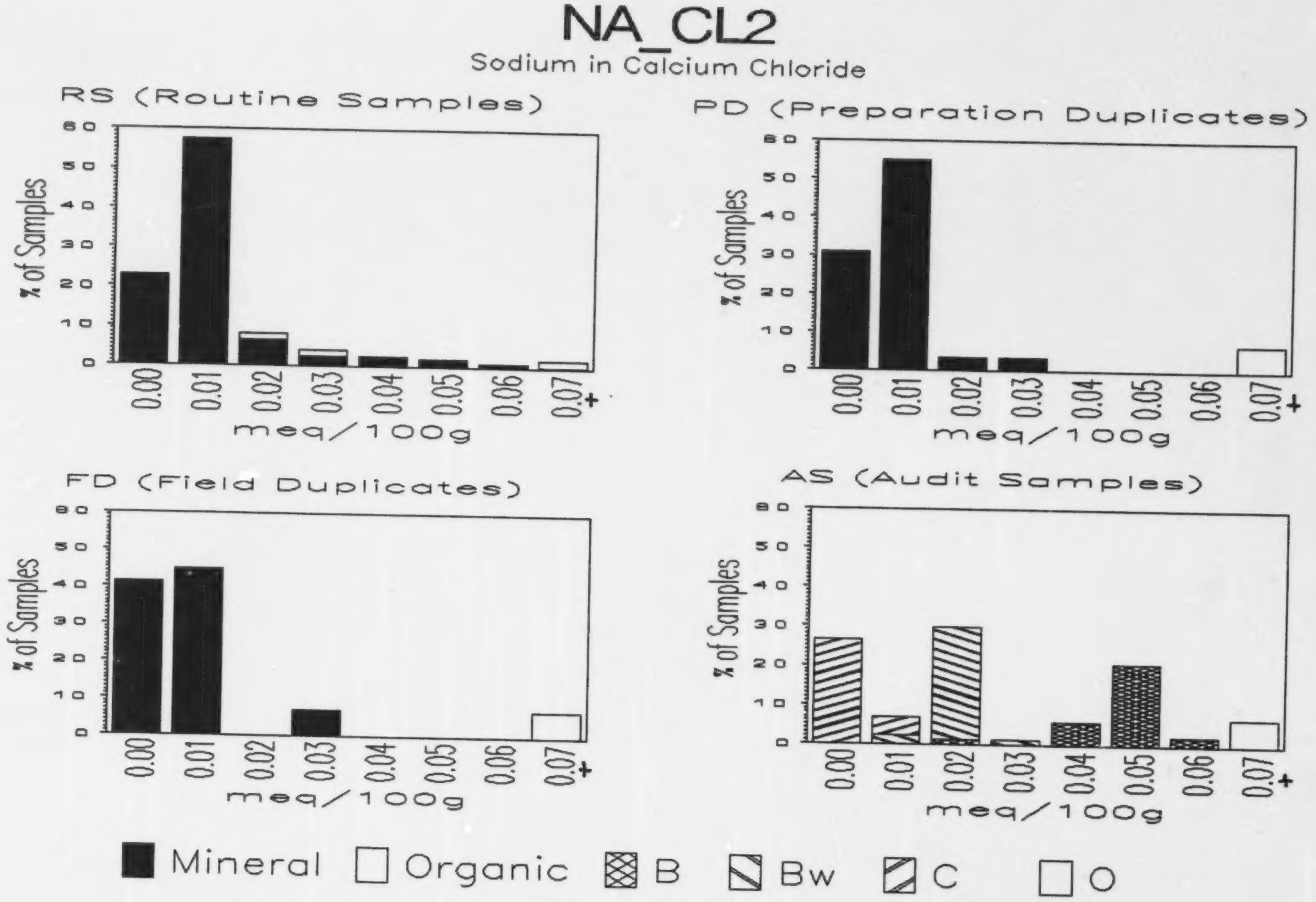


Figure G-30. Range and frequency distribution for NA_CL2.

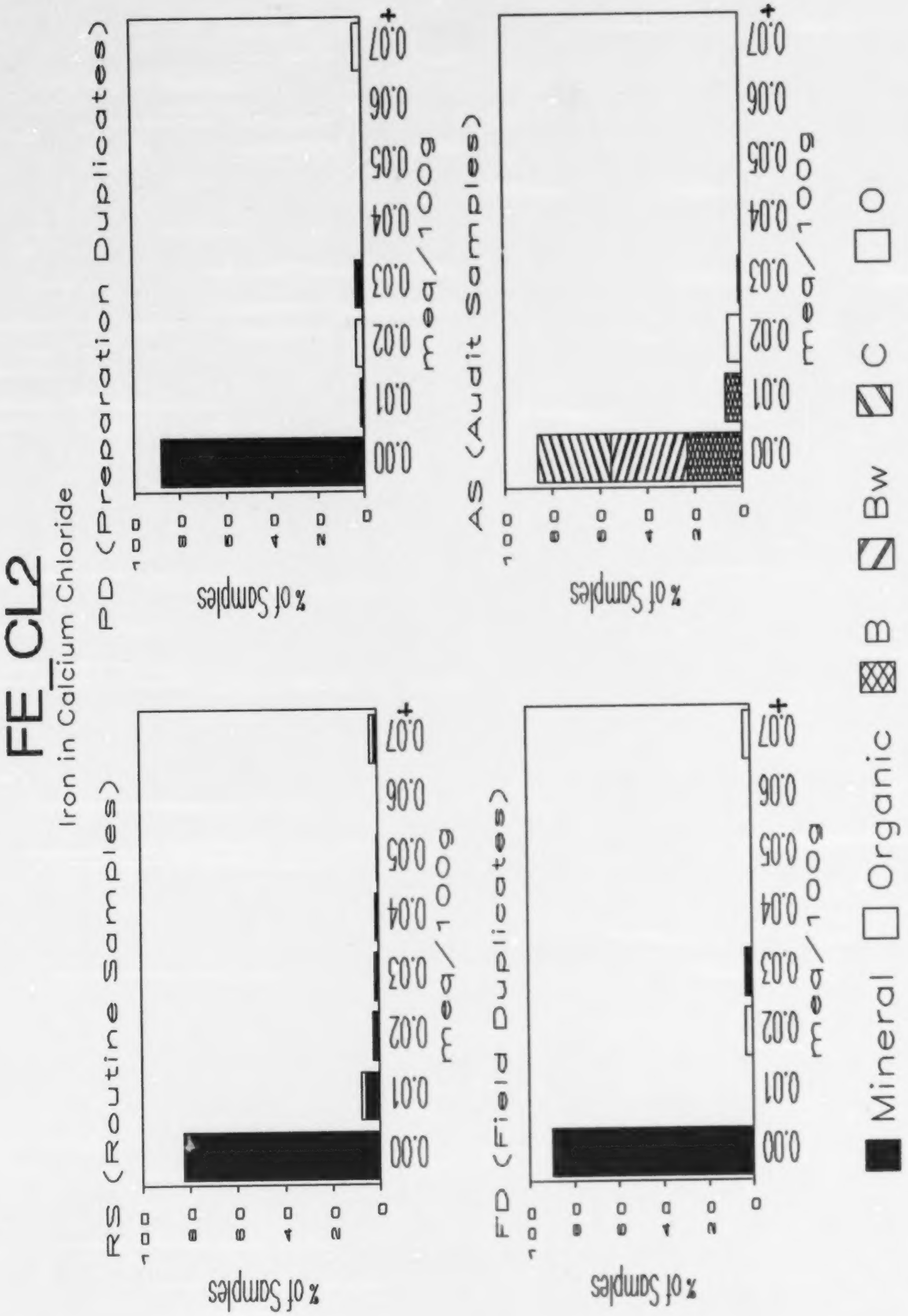


Figure G-31. Range and frequency distribution for FE_CL2

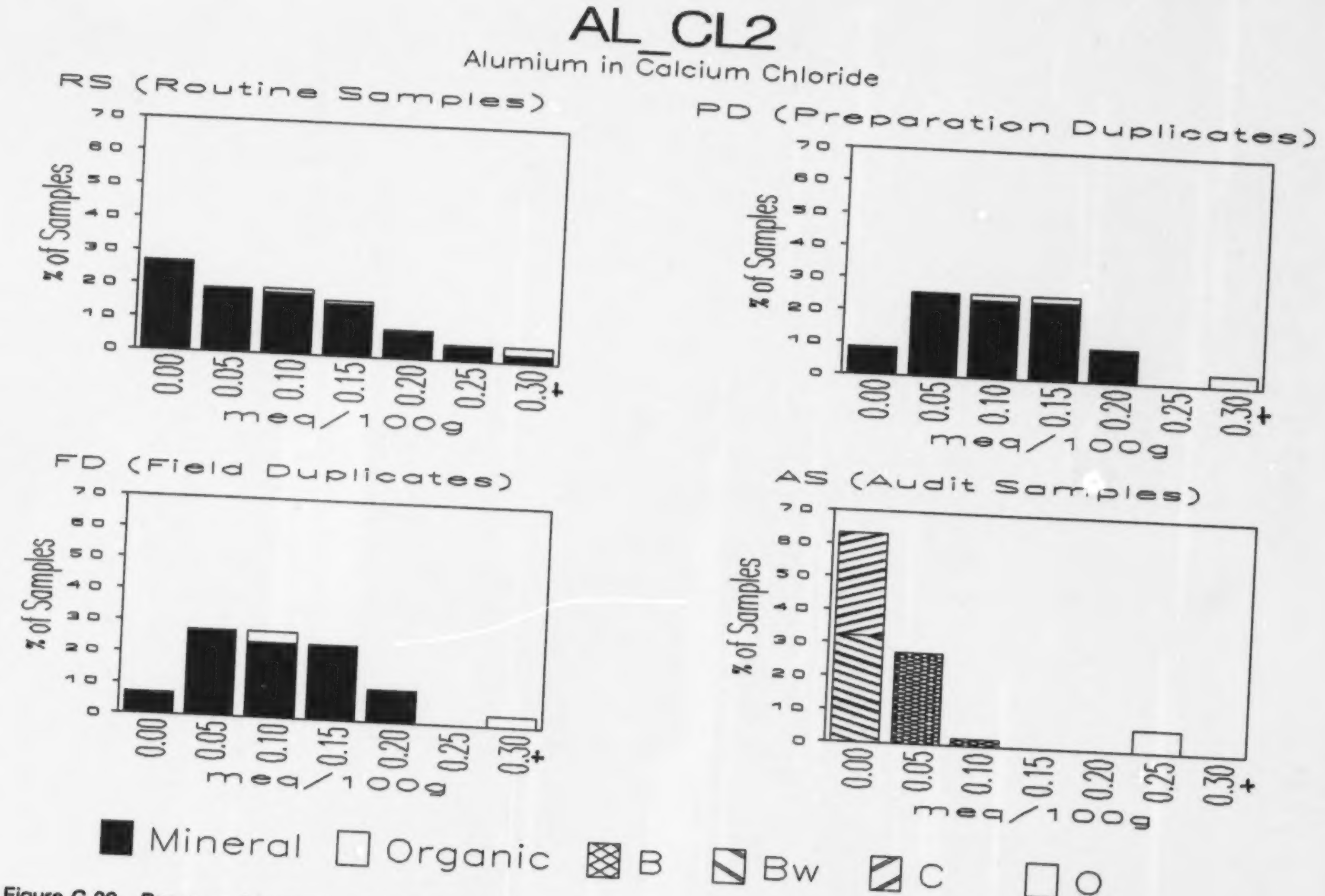


Figure G-32. Range and frequency distribution for AL_CL2.

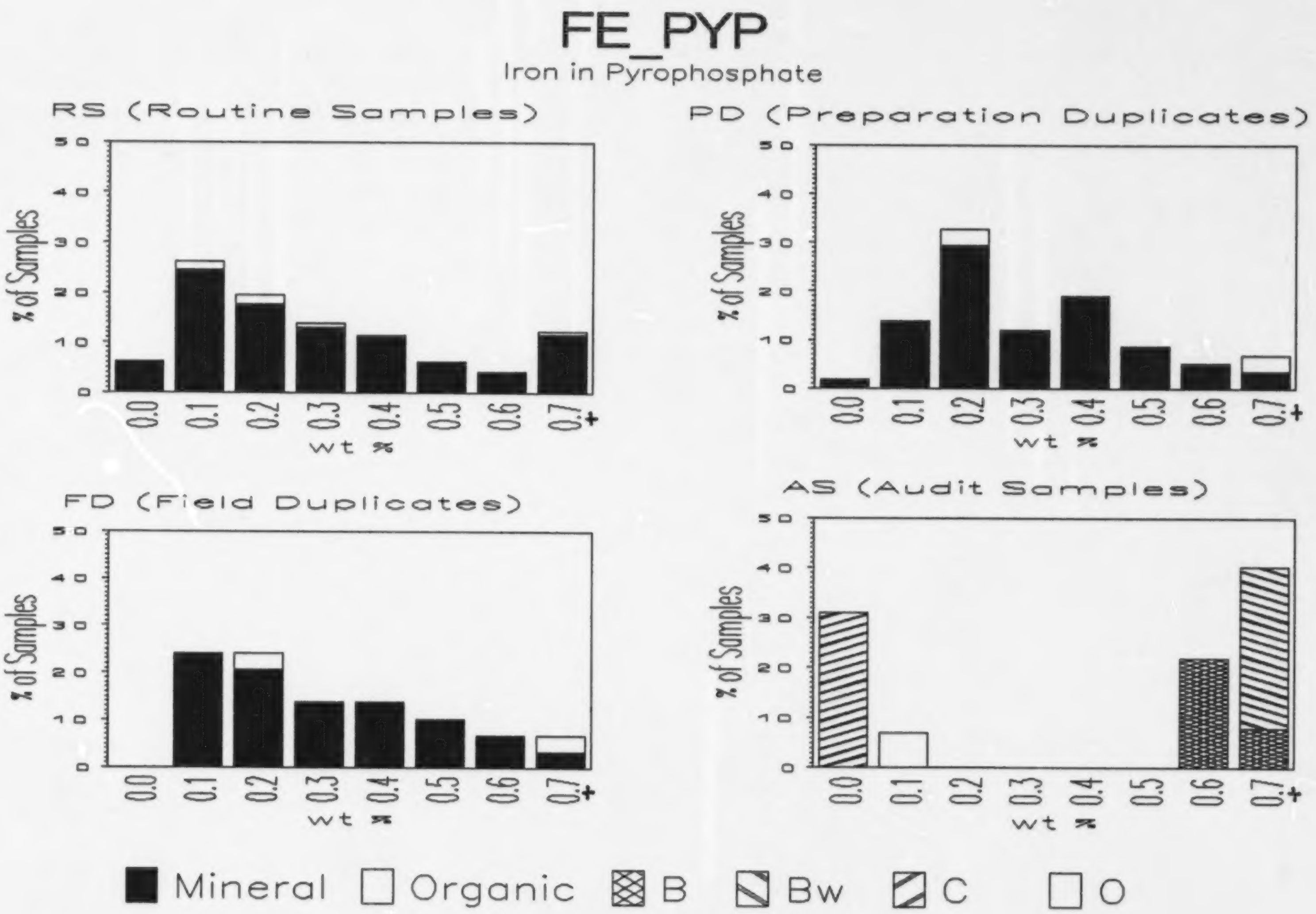


Figure G-33. Range and frequency distribution for FE_PYP.

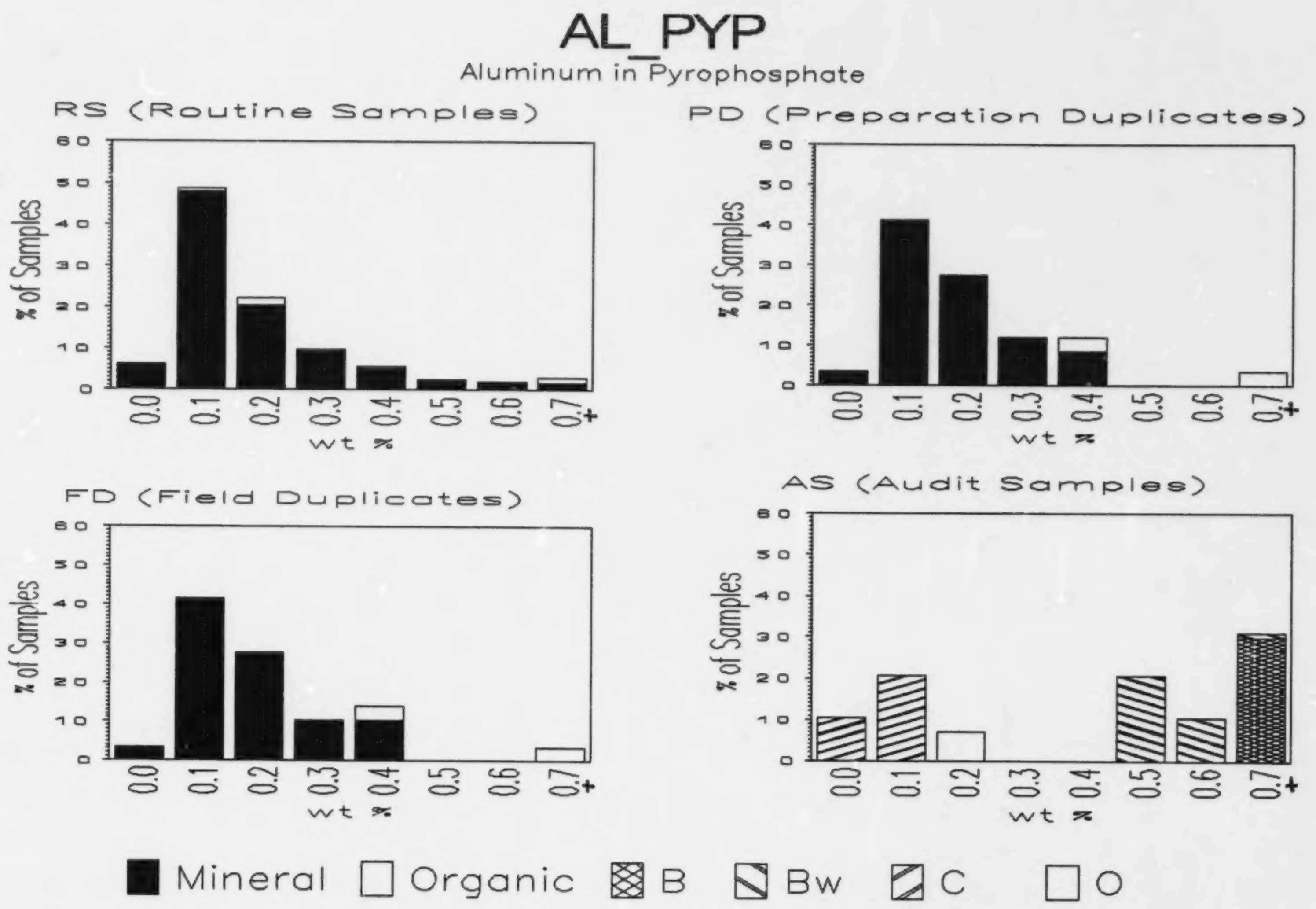


Figure G-34. Range and frequency distribution for AL_PYP.

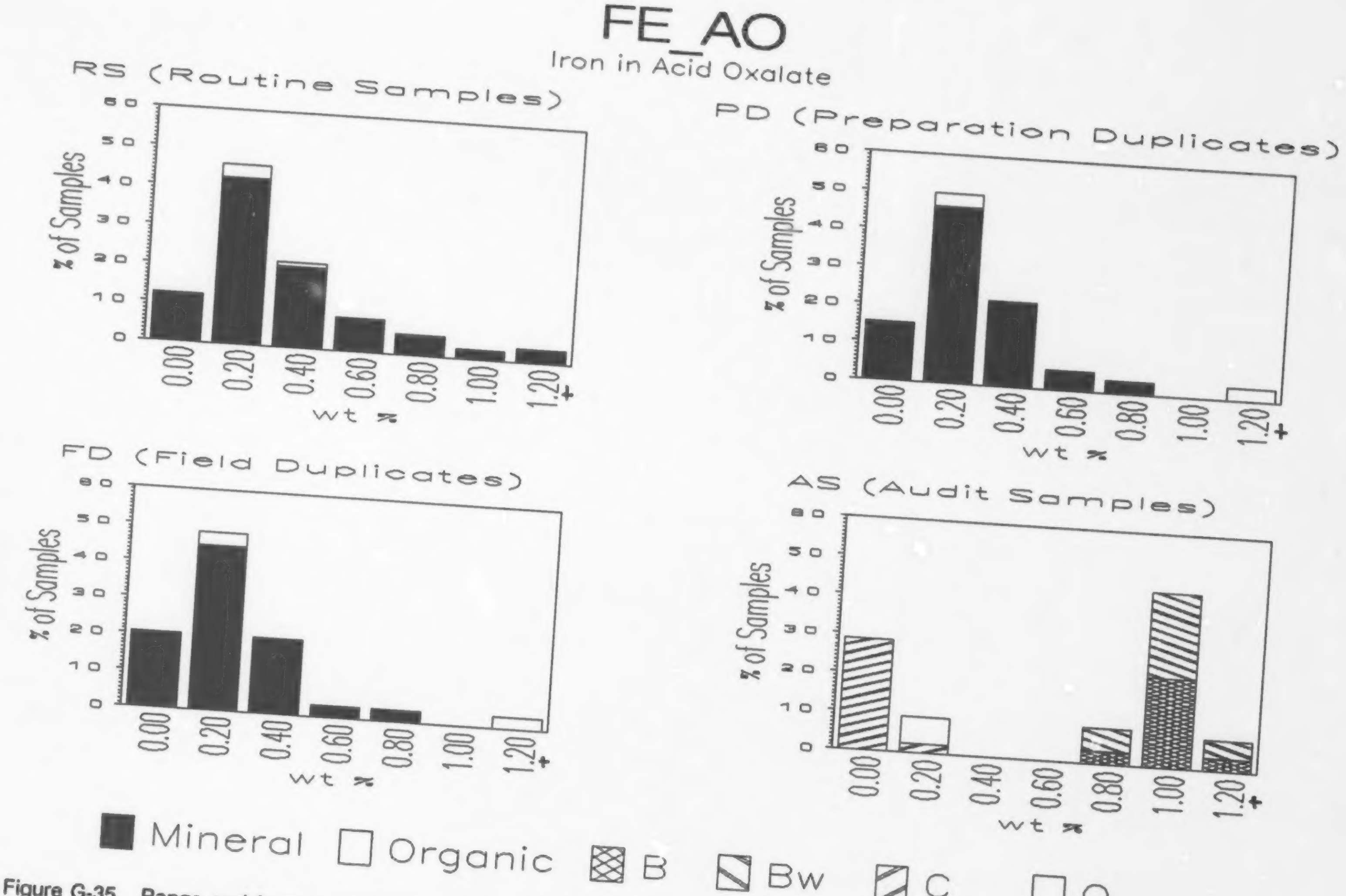


Figure G-35. Range and frequency distribution for FE_AO.

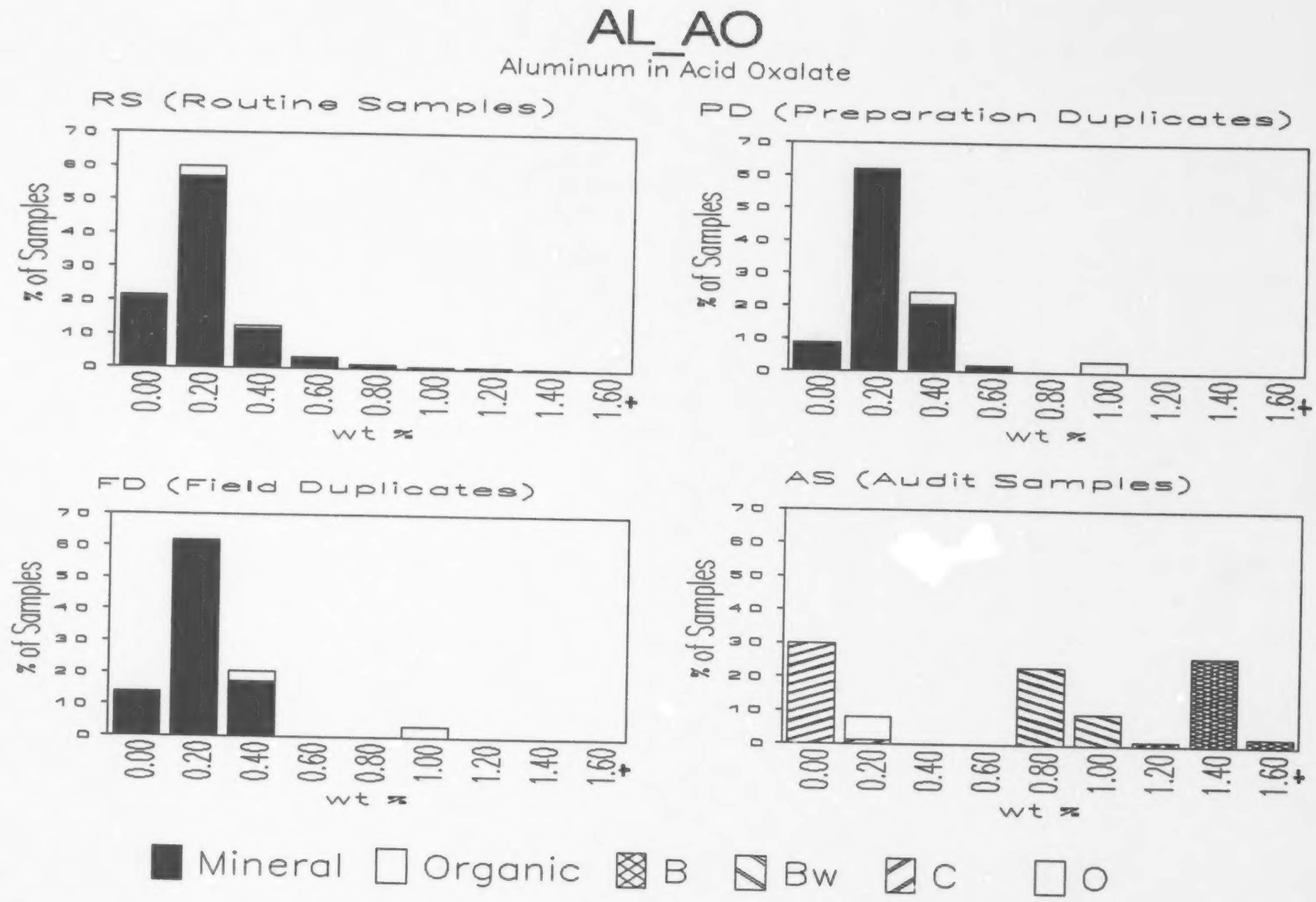


Figure G-36. Range and frequency distribution for AL_AO.

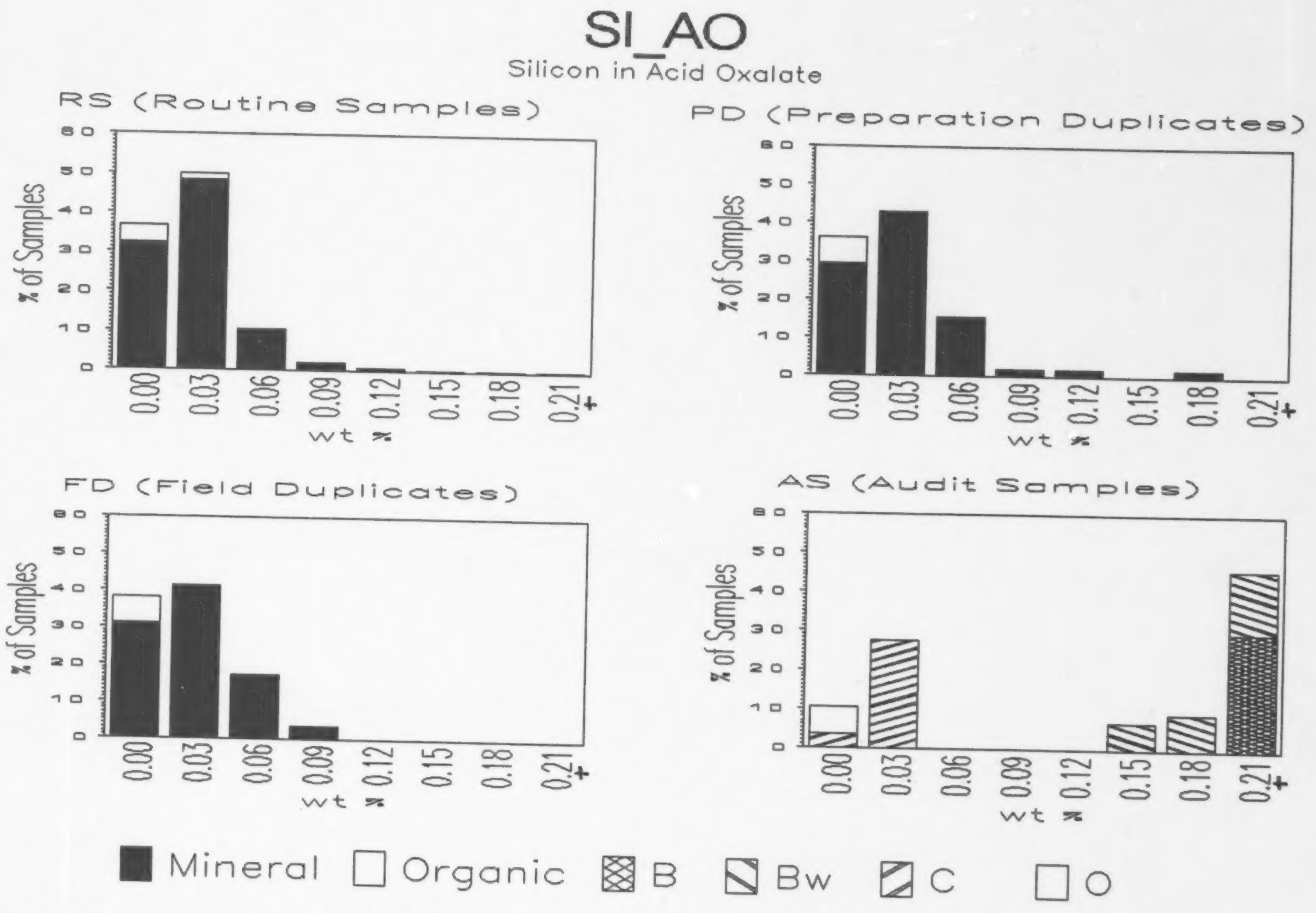


Figure G-37. Range and frequency distribution for SI_AO.

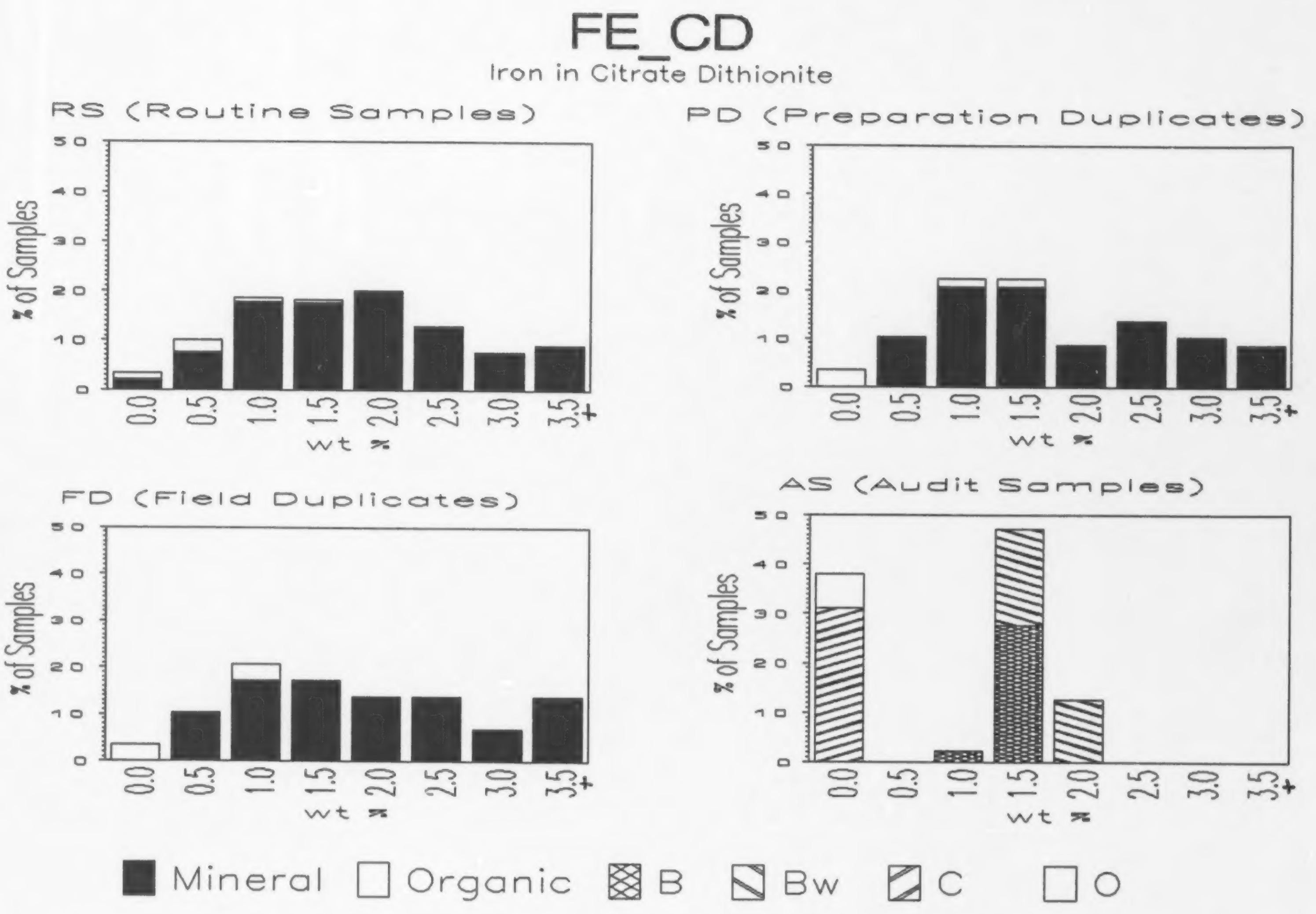


Figure G-38. Range and frequency distribution for FE_CD.

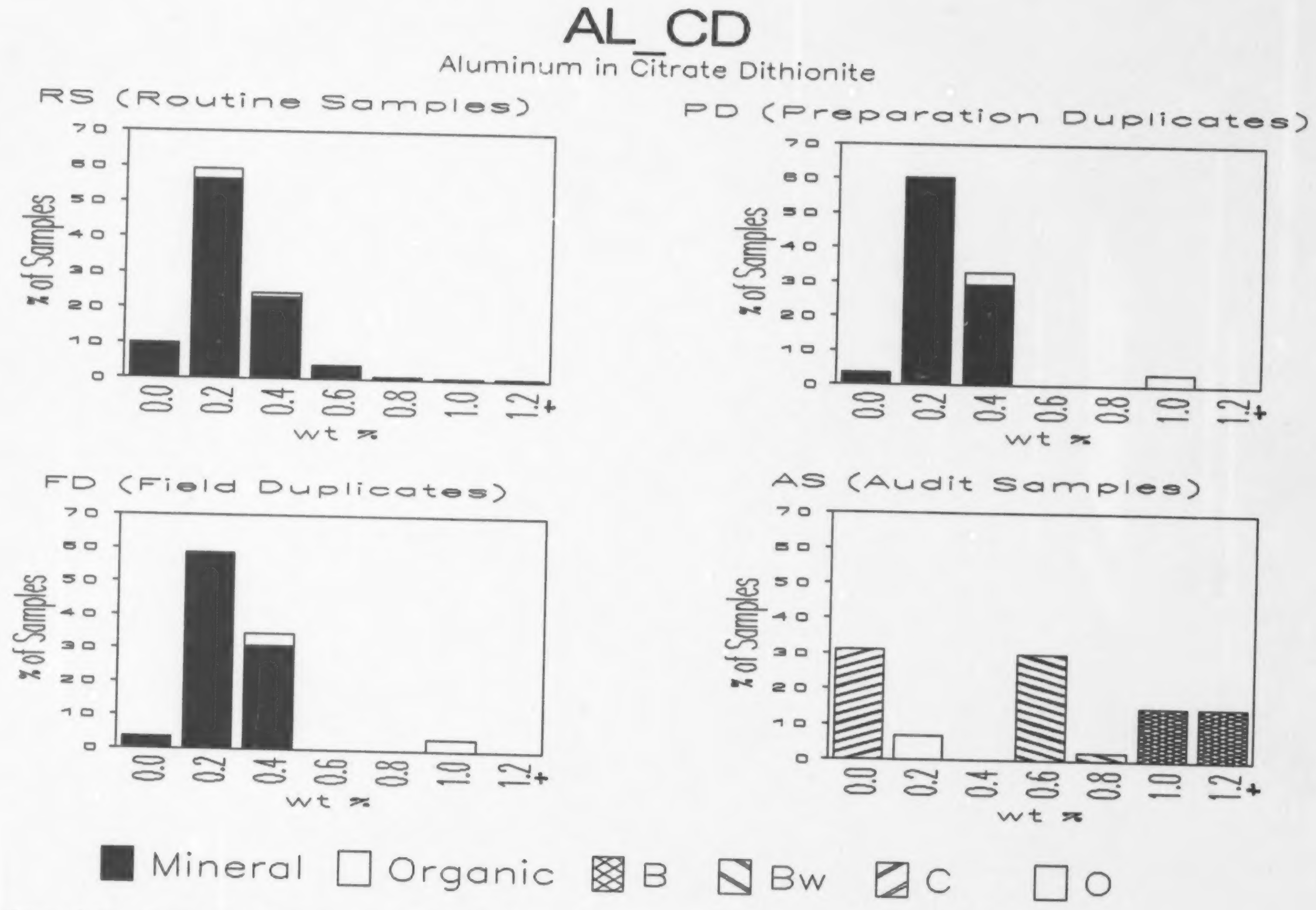


Figure G-39. Range and frequency distribution for AL_CD.

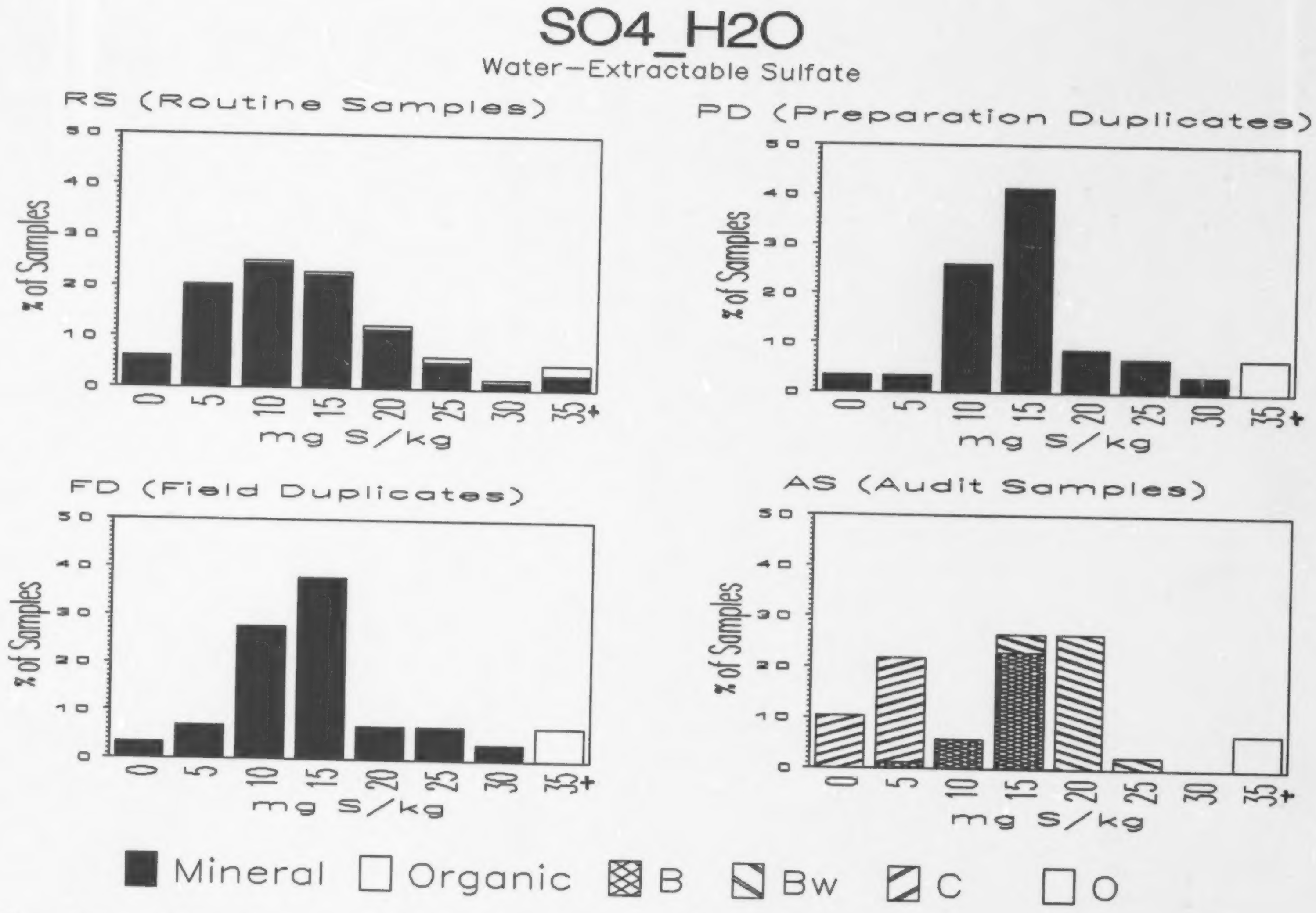


Figure G-40. Range and frequency distribution for SO4_H2O

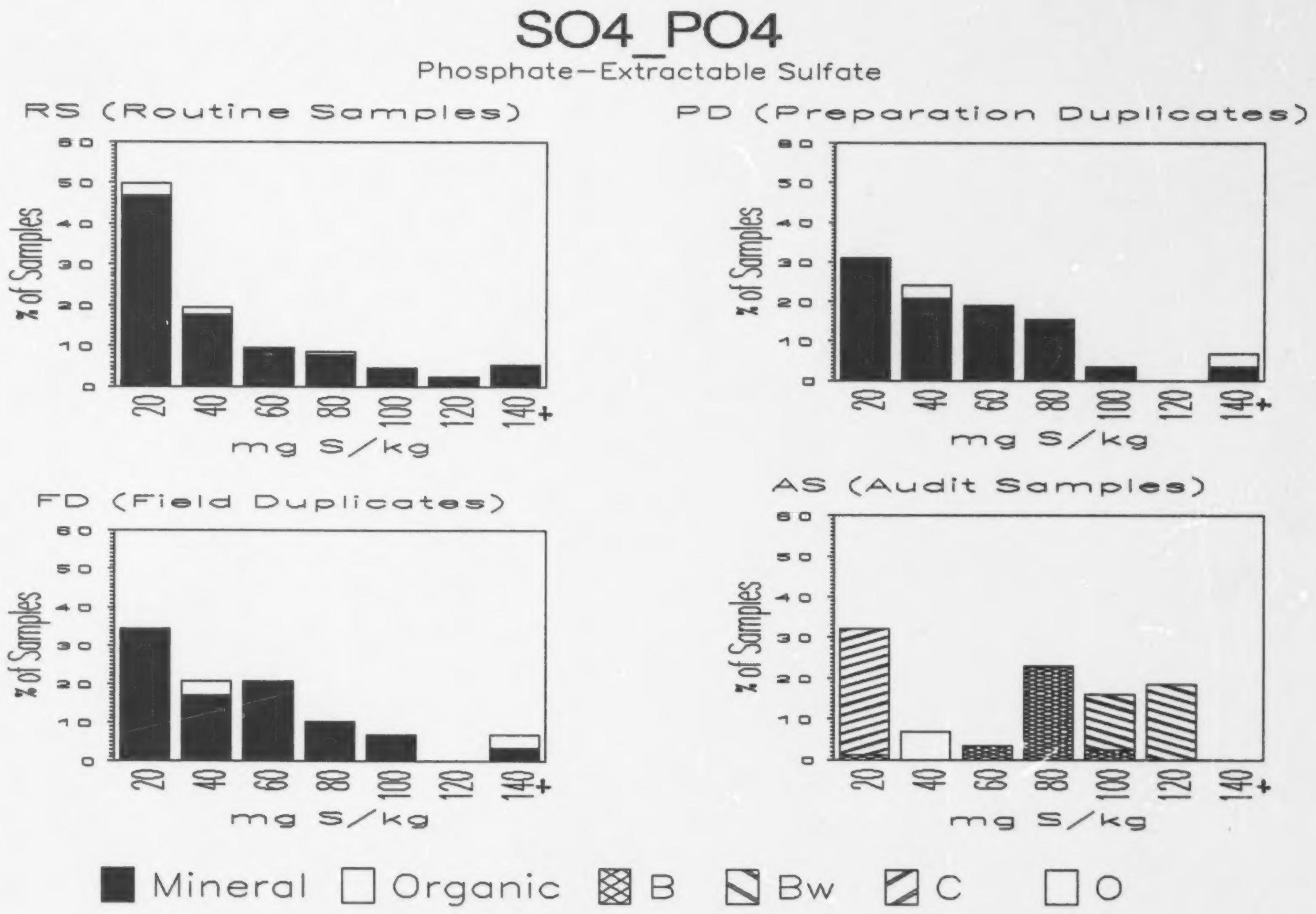


Figure G-41. Range and frequency distribution for SO4_PO4.

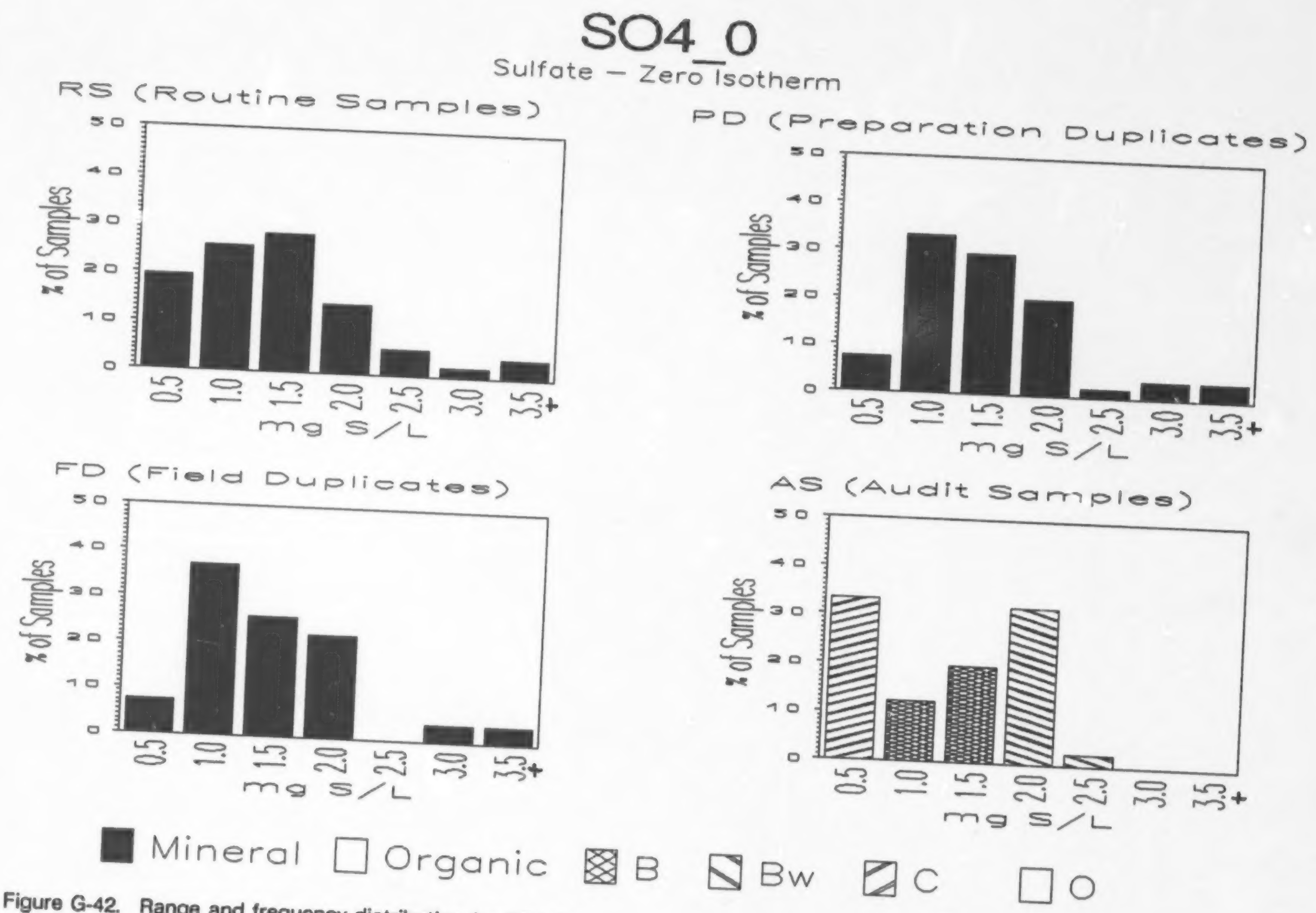


Figure G-42. Range and frequency distribution for SO4_0.

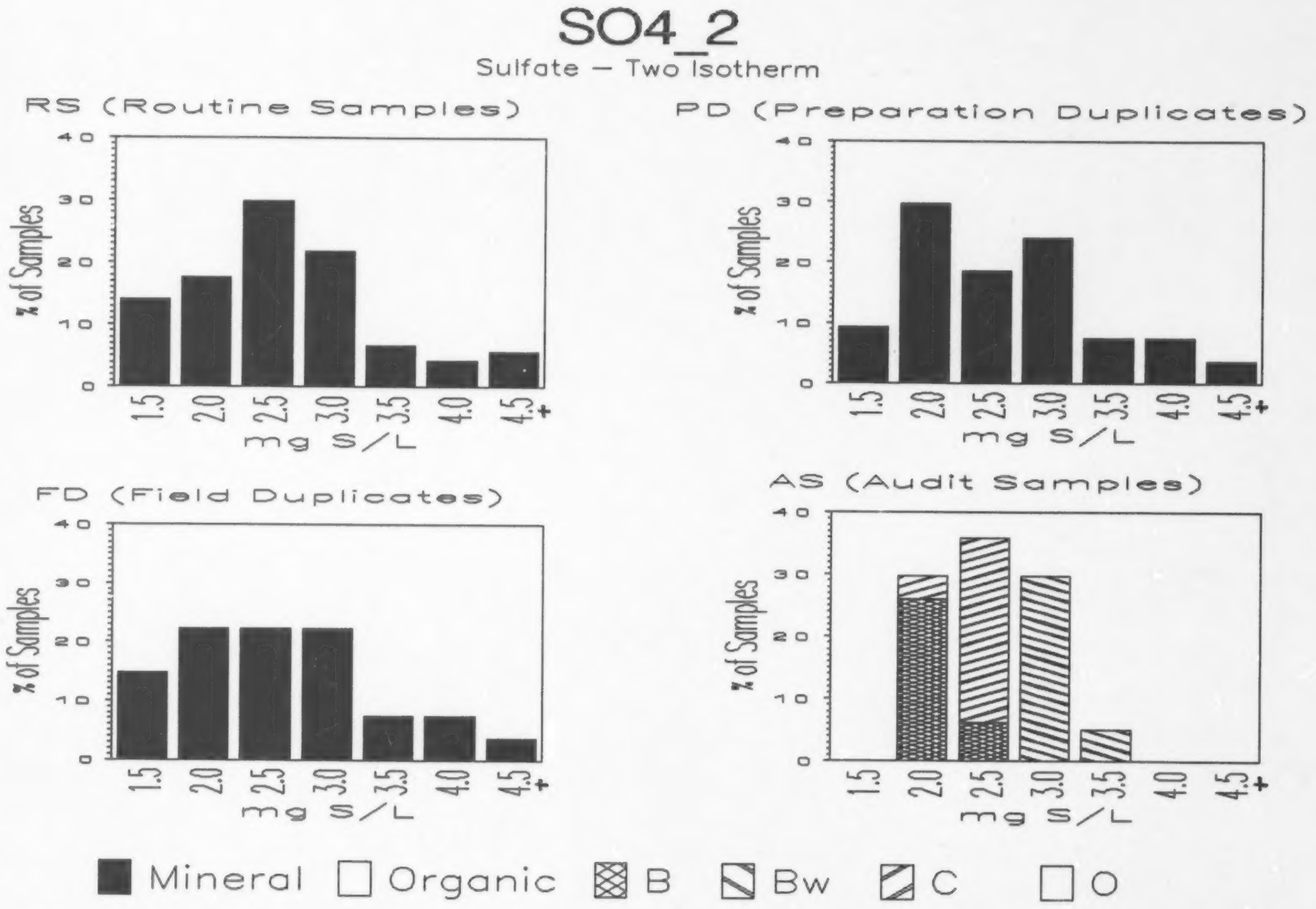


Figure G-43. Range and frequency distribution for SO4_2.

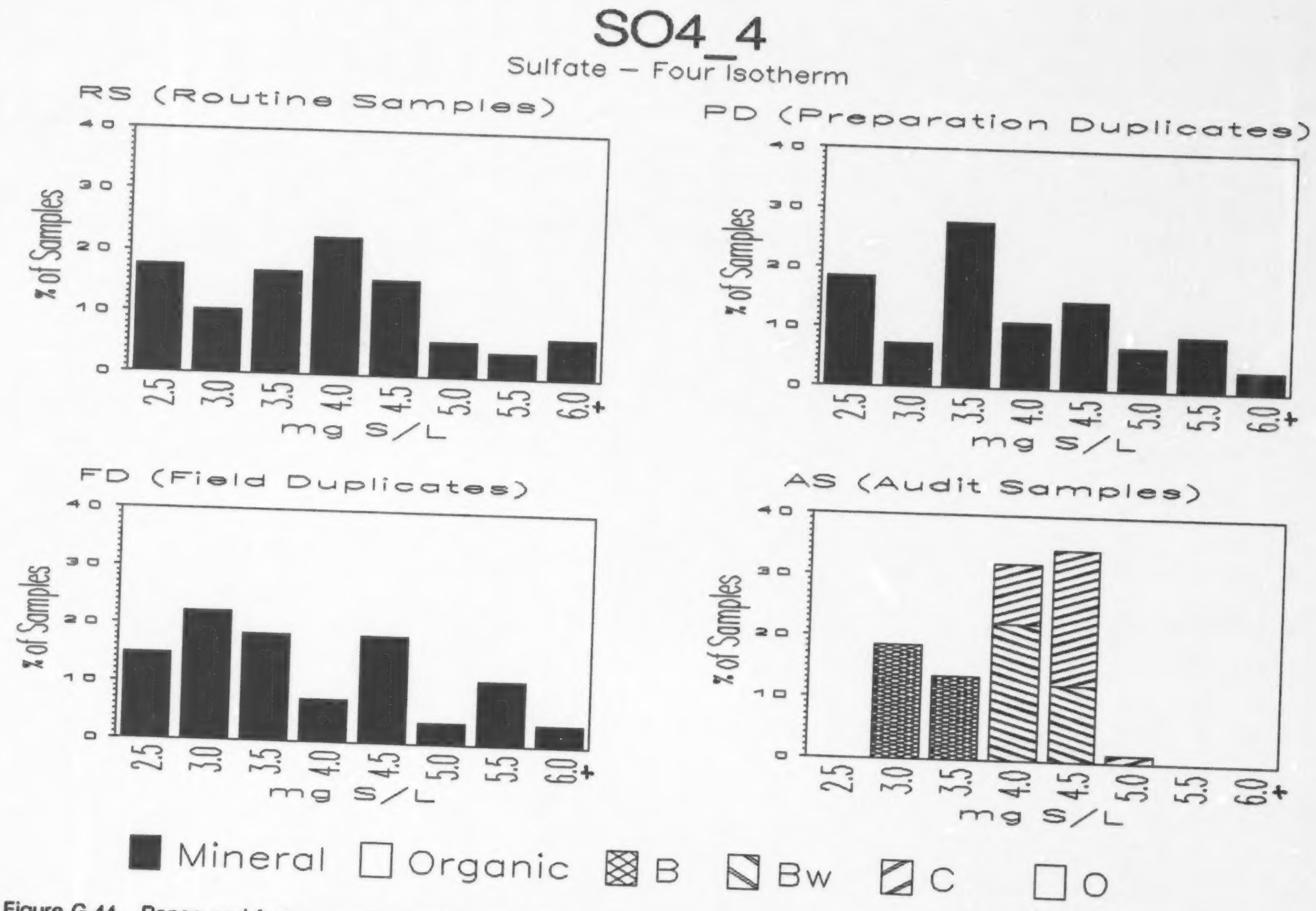


Figure G-44. Range and frequency distribution for SO4_4.

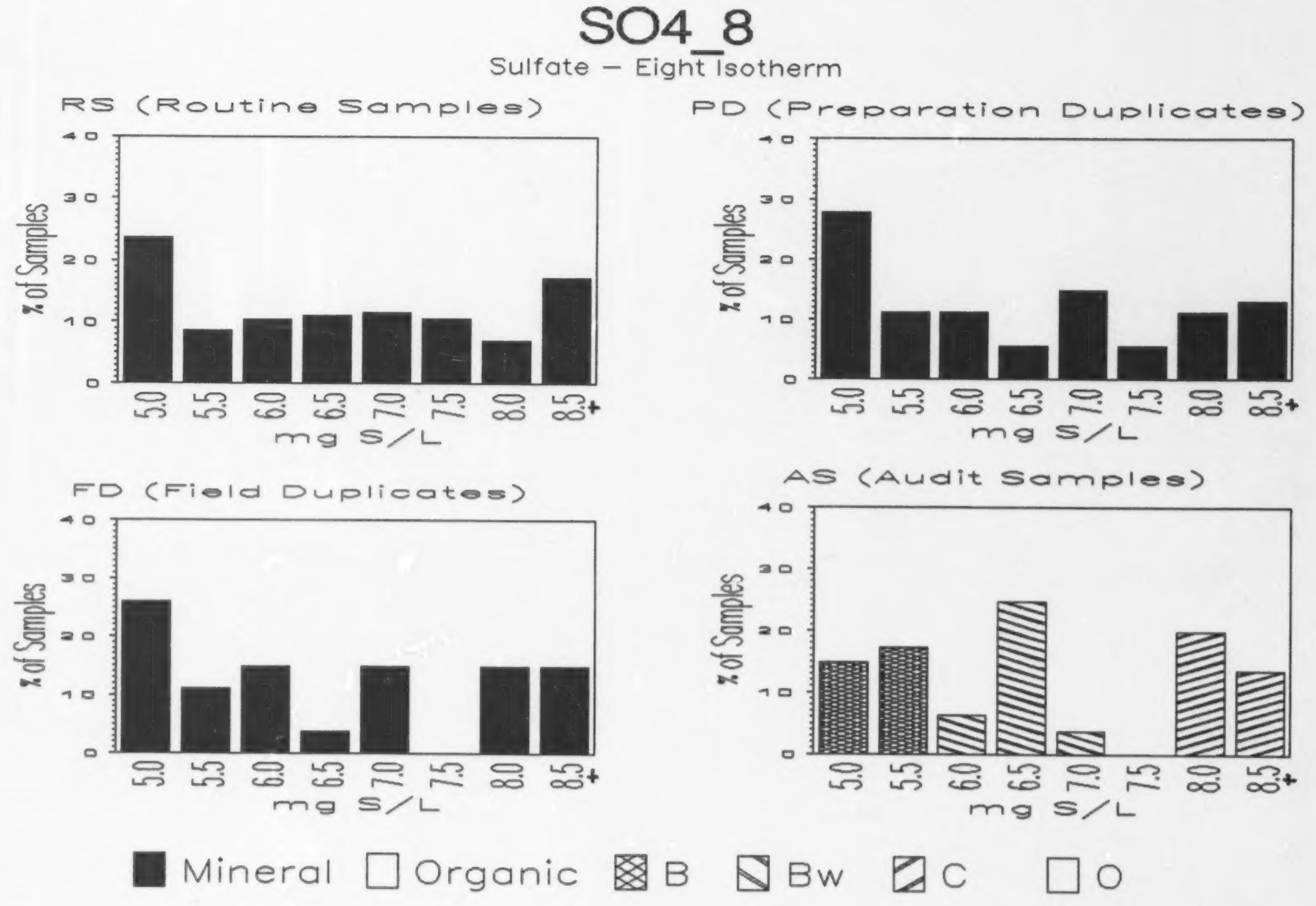


Figure G-45. Range and frequency distribution for SO4_8.

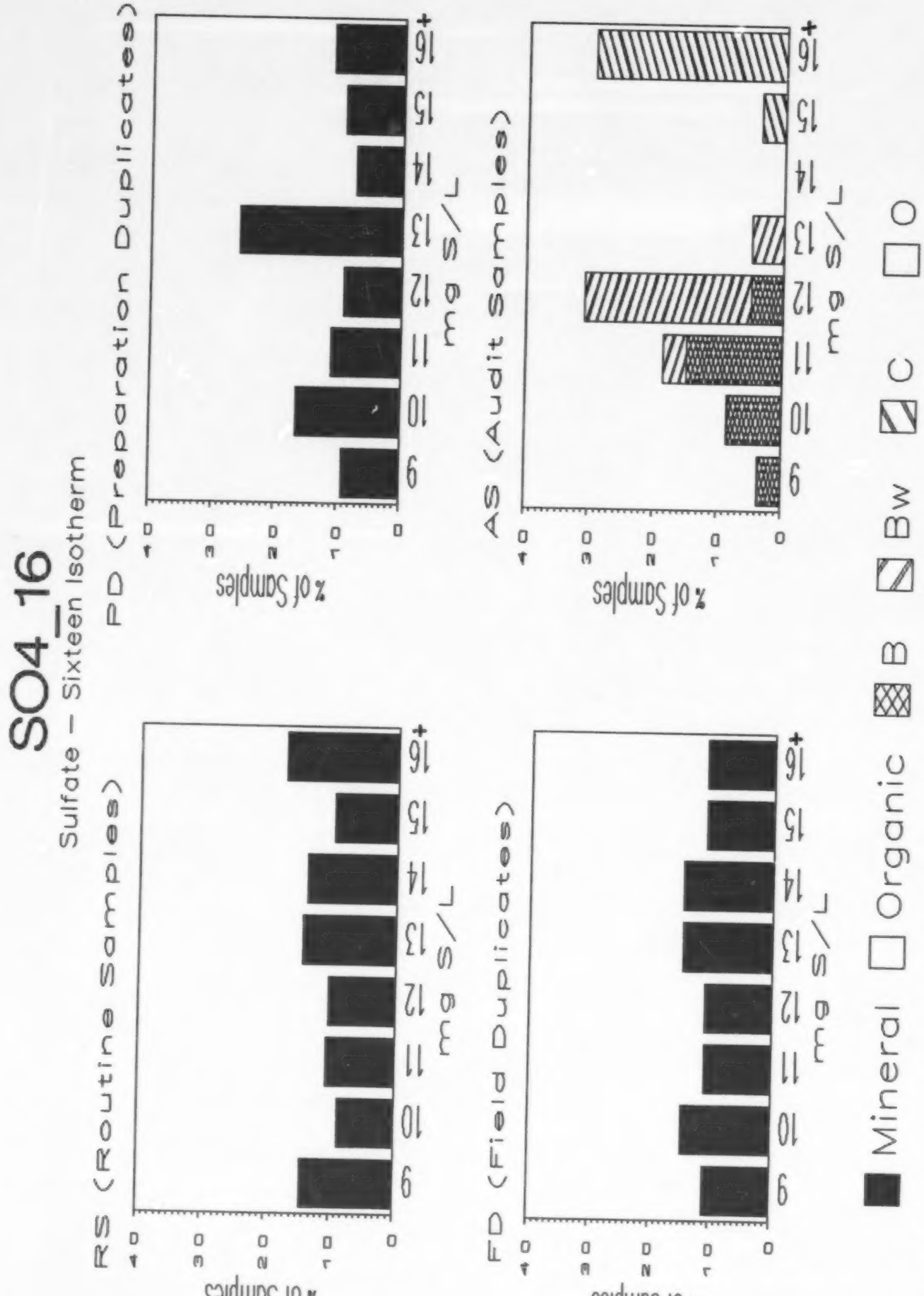


Figure G-46. Range and frequency distribution for SO4_16.

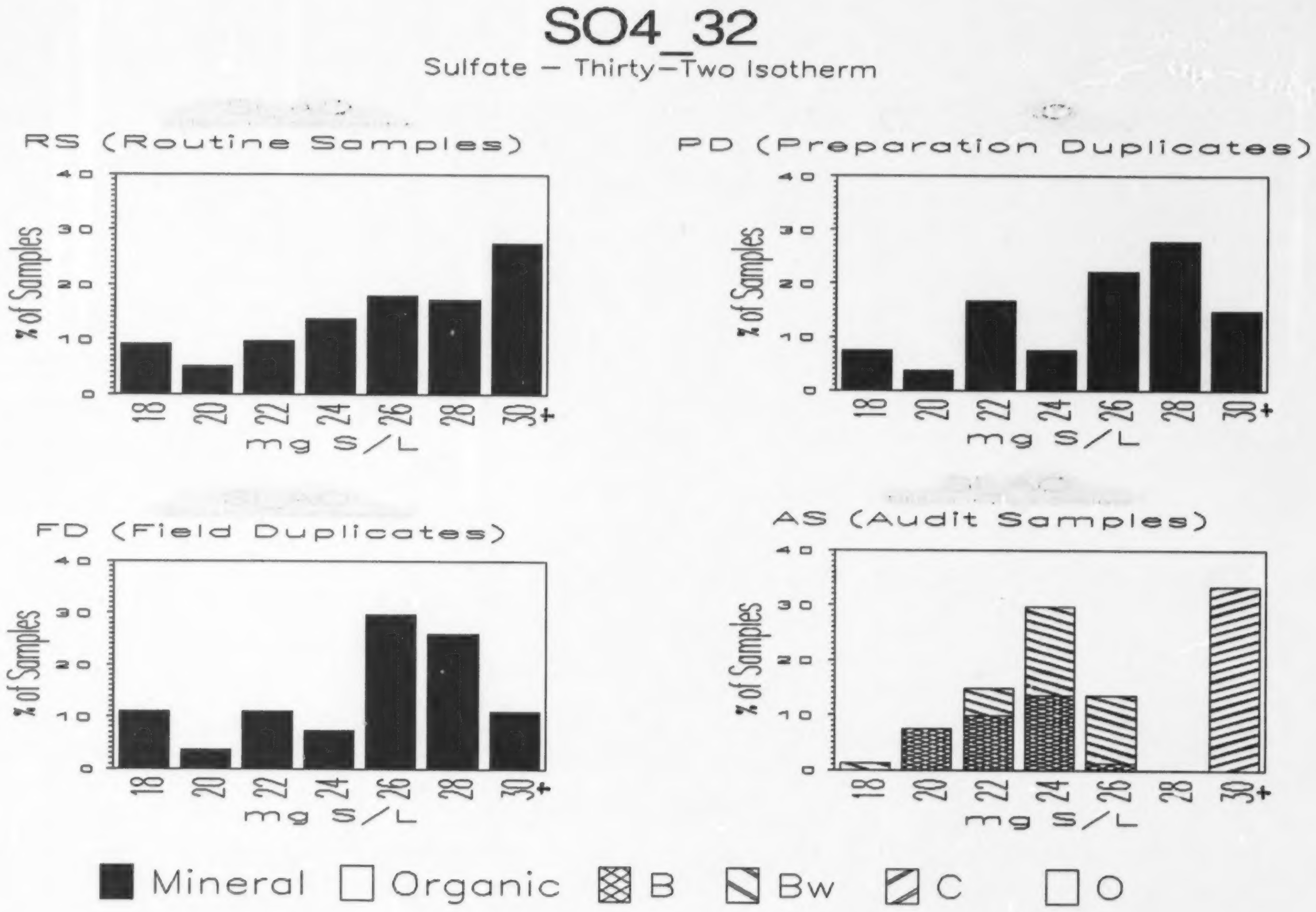


Figure G-47. Range and frequency distribution for SO4_32.

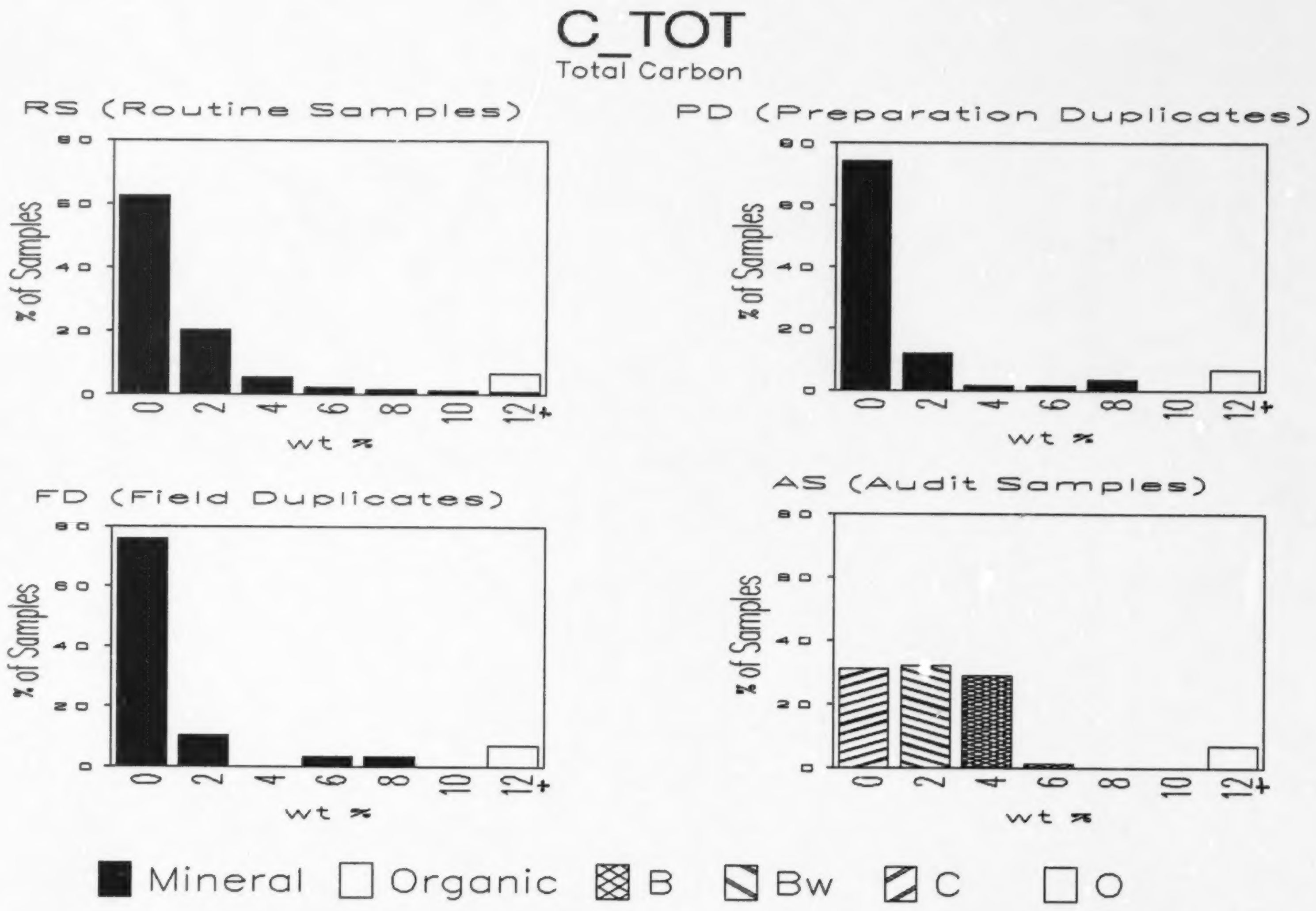


Figure G-48. Range and frequency distribution for C_TOT.

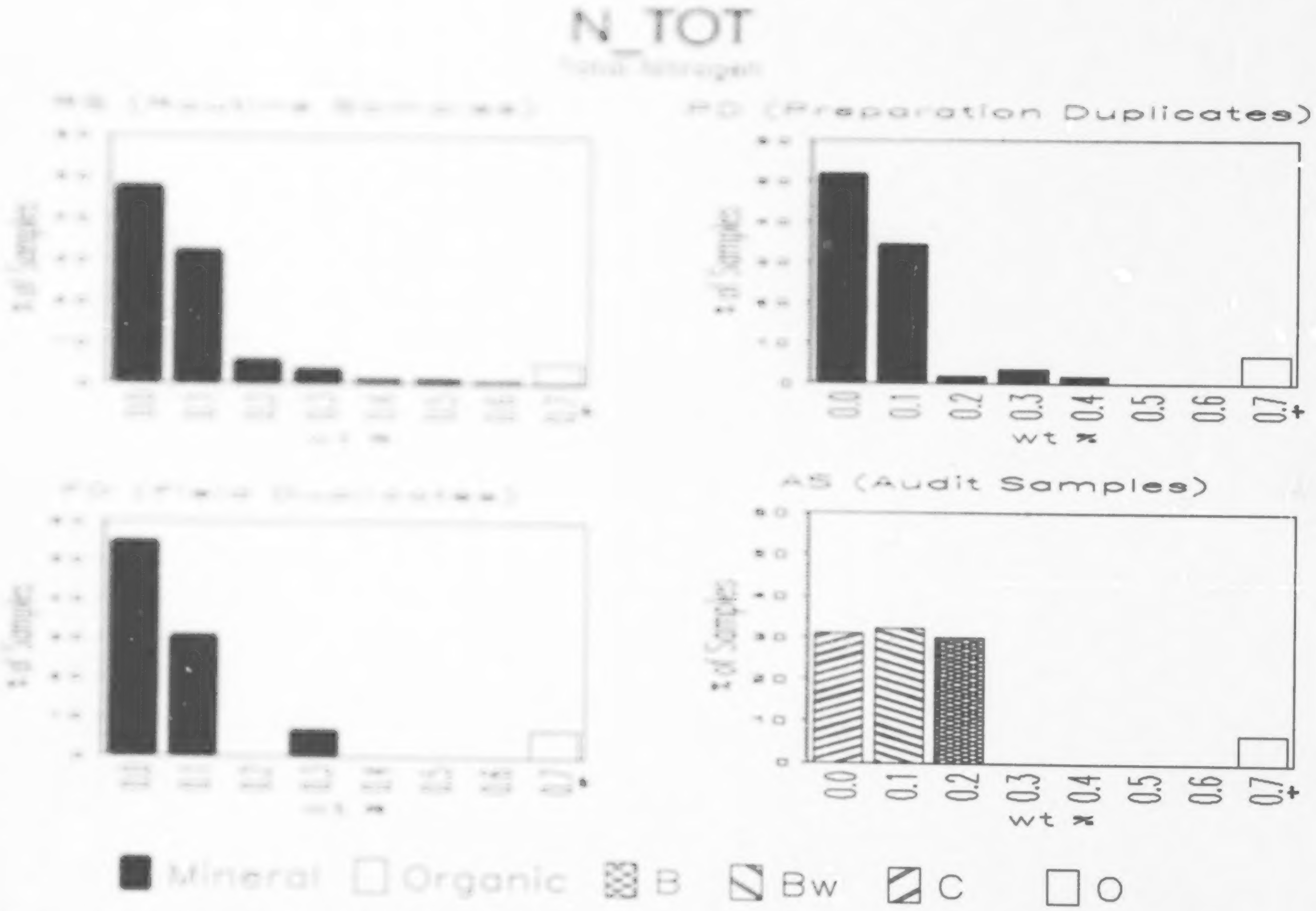


Figure G-48. Range and frequency distribution for N_TOT.

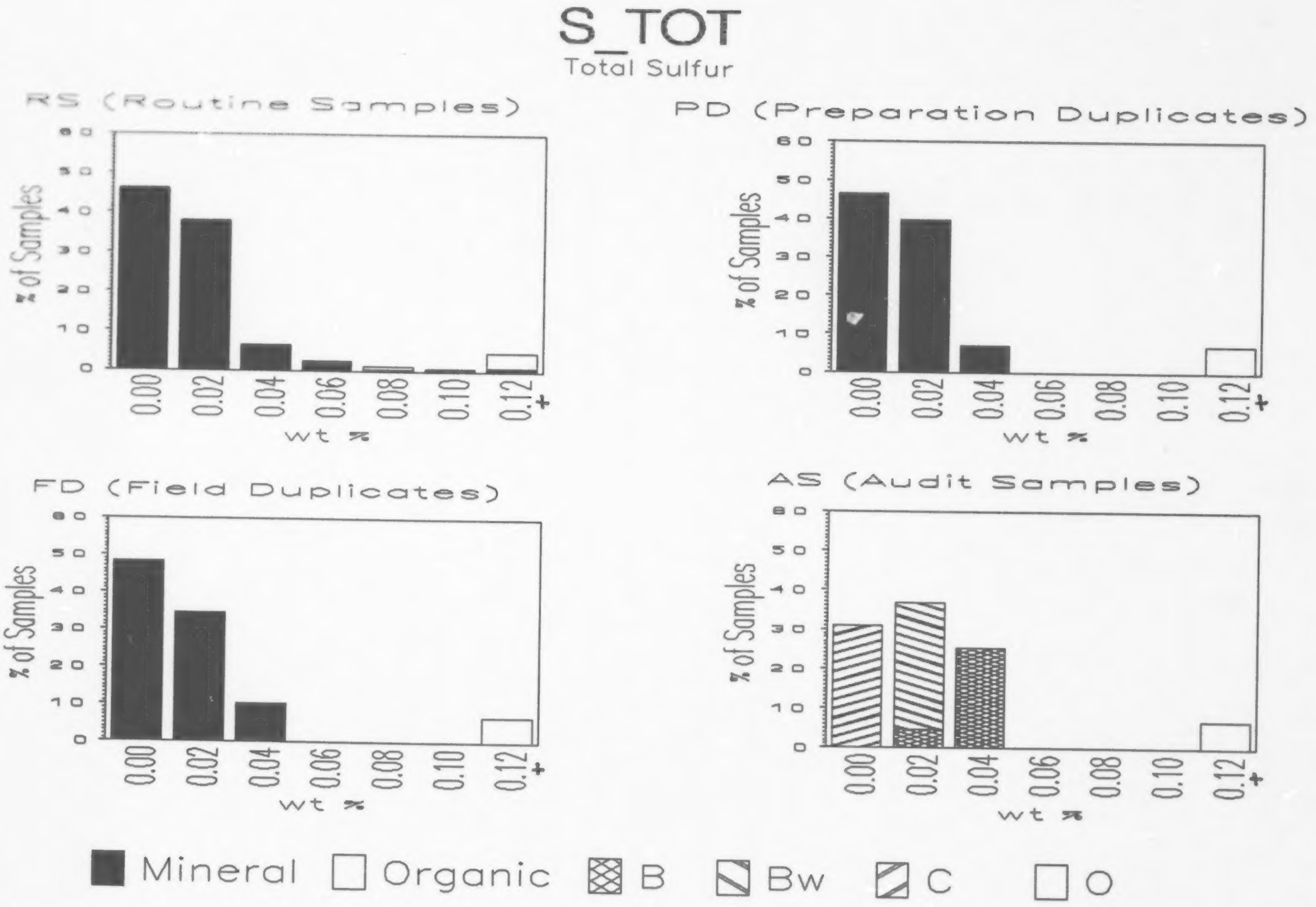


Figure G-50. Range and frequency distribution for S_TOT.

Appendix H

Technical Systems Audit Reports

This appendix contains copies of the reports written by the QA staff audit teams that performed technical systems audits at the analytical laboratories. The reports contain information on laboratory performance, discrepancies identified in the audits, and resolutions to the issues raised. Laboratories are identified only by number in order to protect their anonymity.

AUDIT REPORT FOR LABORATORY 1

Date of Audit: November 17, 1988

Participants: B. Schumacher and R. Slagle - Lockheed-ESC

Report:

The laboratory system audit went extremely well due primarily to the large number of analyses that had been completed by the lab and entered into the LEVIS data entry system and due to a computer program written by R. Slagle which allowed for the rapid determination of data that were outside allowed windows for accuracy and precision. The laboratory personnel were extremely helpful during the data analysis and laboratory evaluation phases of the system audit. All concerns expressed during the pre-award audits had been properly addressed and corrected by the laboratory. Several areas of concerns, problems, and comments were encountered and will be discussed separately relating first the concern and then the potential solutions to the problem.

The first major problem encountered was due to the change in methods for determining CEC and exchangeable cations as extracted by NH_4OAc and NH_4Cl. The lab reported and showed that the method using a polyester pre-plug and the Acrodisc™ in-line filter resulted in extremely slow sample processing or a complete blockage of extraction solution through the soil resulting in an incomplete extraction and thus reanalysis of the sample. The samples in which a solution blockage occurred were not restricted to the high clay soils as was originally suspected. The lab requested a resolution of the problem before November 24, 1988 so that the first batch could be competed by the end of the month.

The second major problem encountered was with the $BaCl_2$-TEA extractable acidity. The reagent and calibration blanks were well below the expected limit as stated in the SOW. Further analyses of the routine data resulted in almost consistent values well below the accuracy windows set for the known audit materials as well as for the lab known QCAS audit sample. Several possible solutions were discussed and are as follow:

1) the original extraction solution was improperly made,
2) the original extraction solution had been exposed to CO_2 resulting in lower than expected buffering capacities (i.e. Ascarite column was not working), and
3) theoretical value of 0.808 meq stated in SOW was incorrect.

Reanalysis of the first batch has been requested due to a failure to meet QA/QC requirements. The laboratory will prepare a new batch of extracting solution to use and will report the quantity of acid required to bring the solution pH to 8.2 in order to determine if the theoretical value is practical.

The laboratory expressed concern that the allowable ranges for the SO_4 isotherm spike solutions were too tight and that to obtain the required values was a hit or miss process even using the same standards. Discussions with P. Shaffer (NSI Technology Services Corp., Inc., Corvallis, OR) were set to be held to check the possibility of loosening the required window with the results being told to the laboratory at a later date.

The laboratory also expressed concern about the influence of method changes on the resultant data for the 0.002M $CaCl_2$ extractions. Their concern was that due to a much greater contact time between soil and solution that the established accuracy windows would not be met as was the case for the QCAS sample. The problem was to be discussed with M. Johnson and P. Shaffer (NSI Technologies, Inc., Corvallis, OR) and answers provided to the lab at a later date.

The lab further expressed concern due to a lack of soil received from the preparatory lab for certain samples. The laboratory manager stated that some samples received only contained about half a bottle of soil.

Several moisture contents were flagged due to weights out of the allowable limits. Reanalyses of the flagged samples was requested.

The water extractable SO_4 replicate value was out of the allowed window (%RSD > 10%). The laboratory was informed that another replicate sample was to be chosen and reanalyzed.

A potential problem was identified for the acid-oxalate extractable Fe and pyrophosphate extractable Al. Three known audit samples were out of the allowable range for both parameters (Fe to the high side and Al to the low side). Discussions are set to be held with L. Blume (EPA - Las Vegas) and M. Papp (Lockheed-ESC) to determine if reanalysis in warranted.

QC charting was discussed with the laboratory with the final result being that the laboratory must produce charts for the QCCS, DL-QCCS, and the QCAS samples.

A list of other concerns was provided to us by the lab and is attached. The concerns primarily relate to changes in methodology among the DDRP soil surveys and whether the changes will influence the accuracy windows that the laboratory must meet. Also attached is a summary listing of the number of samples that were out of allowed accuracy ranges, the parameter, whether the sample value was high or low, and how much the value was out of the accuracy window on the high or low end.

A list of the scheduling for the first three batches with their associated official receipt dates (i.e. their start dates for the 60-day processing period) is as follows:

Batch	Actual Receipt Date	Official Receipt Date
30101	10/18/88	11/7/88
30104	11/1/88	11/17/88
30107	11/17/88	11/21/88

SUMMARY OF AUDIT WINDOW DATA FOR BATCH 30101

Number of samples out	Parameter	High or Low	How much
1	pH_H_2O	high	0.064
4	pH_01M	high	0.99 to 0.15
8	pH_002M	high	all samples at high end of window or over the limit
3	CEC_CL	low	0.03 to 0.372
3	CA_OAC	high	0.015 to 0.028
1	CA_CL2	high	0.003
4	MG_CL2	high	0.001 to 0.009
7	AC_BACL	low	2.157 to 11.465
3	FE_AO	high	0.006 to 0.031
3	AL_PYP	low	0.027 to 0.603
1	C_SAND	high	1.023
1	F_SAND	low	2.07
1	M_SAND	low	0.15
1	C_SILT	high	1.161

Total number of audit samples checked = 11.

AUDIT REPORT FOR LABORATORY 1

Date of Audit: January 25-26, 1989

Participants: M. Papp, G. Byers, B. Schumacher, R. Slagle - Lockheed-ESC,
L. Blume - Environmental Protection Agency, Las Vegas, NV

Introduction

The purpose of this report is to document the major issues and concerns raised at the recent audit of Laboratory 1 which took place on January 25-26, 1989. The goals of this audit were to: (1) assure that the methods and operations as stated in the contracts were being implemented as specified, (2) assess the quality of existing data, (3) follow-up on issues raised at past audits, (4) discuss the process used to evaluate data packages, and (5) answer any questions concerning the contracts.

Audit Report

An introduction was given by L. Blume for the agenda and procedures to be followed during the audit.

The major issues raised at the pre-award audit were reviewed for clarification and progress by Laboratory 1. These issues included (1) unclean AA burner heads due to flame problems, (2) the use of mixed standards for Fe, Al, and Si, (3) the use of a one-point calibration instead of a three-point calibration for atomic absorption (AA), (4) the non-use of temperature calibration for pH, (5) open-bin riffle splitter, (6) and use of welder's grade acetylene for AA instead of commercial grade or better. These issues were discussed and responses indicated that Laboratory 1 had resolved them. Other issues such as expansion of facilities at the laboratory, chain-of-custody procedures, and availability of specified equipment for the DDRP analyses were reviewed.

A discussion followed regarding the first batches of soils that were forwarded for analysis. Analytical issues were discussed after recent printouts of the data were made available by R. Slagle and B. Schumacher.

Finally, a discussion followed on the Laboratory Entry and Verification Information System (LEVIS) with R. Slagle. Topics such as cooperation between personnel at Laboratory 1 and EMSL-LV, transfer of analytical data using LEVIS, the format and requirements of the tables used for the analytical data, and some calculation and reporting unit concerns were reviewed.

The audit team held a private caucus to evaluate specific issues prior to more discussions with Laboratory 1 personnel. Included topics were:

(1) QC Charting and QC samples, e.g., missing QCAS and DL-QCCS data, data identification on the axes, the suggested use of the same stock solution DL-QCCS throughout the survey, documentation of the DL-QCCS changes, and missing IDL data.

(2) Data analysis, e.g., specific problems in batches 30101, 30104, 30107, and 30110 regarding confirmation of data, reanalysis of Ca, Mg, SO4 and pH parameters in various extractants.

A laboratory tour was conducted for the audit team. Specific issues were discussed regarding instrumentation by inductively coupled plasma (ICP) and AA analyses. One specific problem was resolved. Standards and samples were run twice through the ICP on similar extracts for which standards were prepared separately. It was recommended that the standards be combined to save analytical time and reduce errors. Possible contamination by using the parafilm in the agitation step was discussed. The location of the laboratory gases and other safety issues, standards, dilutions, integration times, wash sequences, etc., for the various instruments were also reviewed. The facilities for sample preparation and holding areas, sample analysis for chemical and physical parameters, and sample storage repository were visited.

A debriefing to Laboratory 1 personnel was conducted the next morning on the data review resulting from the audit team caucus. The issues were thoroughly discussed. More specifically, problems with the cations in acetate and chloride, the sulfate in phosphate spike solution specified was too tight, sulfate in water was out of 10% RSD window, the moisture content flags, iron and aluminum in acid oxalate and pyrophosphate were out of the accuracy windows, the acidity in barium chloride-TEA results were too low. Also, the pre-plug plus disc restricted the filtering and modifications would be forthcoming. An insufficient quantity of soil was received for certain samples and this was to be rectified. The change in the procedure for the calcium chloride resulted in not able to meet the accuracy windows. The QC charts have to be provided to EMSL-LV.

A presentation was made by the audit team on the reanalysis template by B. Schumacher and G. Byers and on the soil chemistry relationships, and control charts on blind samples across all laboratories by M. Papp. This was presented for the benefit and information of Laboratory 1 personnel attending the audit.

Closing remarks and a summary were given by L. Blume.

Agenda for the systems audit for Laboratory 1

1/25/89	
2:00-3:00 pm	Introduction and discussions
3:00-4:30 pm	Audit team caucus to evaluate the following requested information: control charts, QCAS, QCCS, DL-QCCS, detection limit raw data, batch 30107 routine data
7:00 [illegible] pm	Laboratory Tour
1/26/89	
9:00-10:30 am	Debriefing to laboratory personnel on data review findings
10:30-12:00 am	Presentation to Lab personnel on: reanalysis template, soil chemistry relationships, control charts of blind samples across all laboratories, true value QCCS for particle size analysis
12:00-1:15 pm	Lunch
1:30-3:30 pm	Discussion and closing remarks

AUDIT REPORT FOR LABORATORY 1

Date of Audit: May 4, 1989

Participants: B. Schumacher and M. Papp - Lockheed-ESC
L. Blume - United States Environmental Protection Agency

Report:

The audit was used mainly to discuss Laboratory 1 billing of miscellaneous expenses and to back up and retrieve the computer hardware and software provided to the laboratory for the endurance of the contract.

Billing:

Discussions were held on the equitable billing of certain items by Laboratory 1. The laboratory did not account for items modified from the original contract that EPA felt made the analysis of a parameter less difficult, thereby reducing the cost of such analysis. The parties decided that Laboratory 1 deduct any of their miscellaneous requests from the billing which had not already been approved and paid.

System Backup:

B. Schumacher received the remaining of official copies of the form 500's. Batch 30125 was corrected for an invalid submission. The batch was then accepted.

B. Schumacher and the laboratory manager then proceeded to back up the entire database. Floppies of the system were created and all hardware was boxed for shipping to Lockheed-ESC.

Since all batches for Laboratory 1 had been accepted, no formal laboratory tour or data review was necessary.

Sample Shipment:

Two batches, 30104 and 30125 were prepared for shipment to EMSL-LV. These batches will be sent to Laboratory 3 for reanalysis of certain Ca and Mg parameters. The remaining batches at Laboratory 1 will be sent to EMSL-LV during the week of 5/8.

AUDIT REPORT FOR LABORATORY 2

Date of Audit: November 15, 1988

Participants:
L. Blume - United States Environmental Protection Agency
B. Schumacher, R. Slagle - Lockheed-ESC

Report:

An on-site audit of Laboratory 2 was conducted on November 15, 1988 by L. Blume, B. Schumacher, and R. Slagle. The purpose of this audit conducted during the first month of analyses was for the following reasons:

1. Verify that all issues of concern identified during the pre-award were corrected.
2. Discuss, identify, and possibly resolve any methods inconsistencies, data analysis errors, etc.
3. Resolve any issues pertinent to LEVIS. Test modem transfer of data to EMSL-LV.
4. Discuss issues pertaining to sample scheduling and contract clarification.

1. Pre-Award Issues

a. Stock solutions working standards

They had a separate table for all DDRP standards. Also had new solutions made that were dated with shelf life and receipt times. New standards will need to be made.

b. Eppendorf automated pipetters needed calibration

The pipettes were not properly calibrated. A recalibration was assured.

c. Instrument logs

Observed they were updated more frequently.

d. Magnesium sulfate reagent

Magnesium sulfate was old (1986) and not desiccated. A new source of $MgSO_4$ reagent was on order and will be used with the first batch.

e. Transport of soils to WAL

WAL will analyze all 0.002 M $CaCl_2$ analytes except K, and the extractable FE and AL samples. In addition, tracking and custody forms would be used for transport.

f. Particle size analysis (PSA)

PSA will be done in a temperature controlled room and temperature will be monitored in a blank (DDI water) cylinder.

g. WAL facility

New benchtops will be added, thereby separating working areas and overall cleanliness was improved.

2. Methods Issues and Data Evaluation

Only detection limit data and pH were available due to the fact the lab was just beginning analyses.

a. CEC filtration problem

Problem - Clogging of samples prevented extraction with NH_4Cl in samples 2.13,17,21 (red audit Bt2)

- Further clogging noted during ethanol rinse in sample 9,10,11,12

Notes - Clog occurred in preplug for NH_4Cl and possibly ethanol

- Removal of Acrodisc in-line filter allowed for easier ethanol rinse although some breakthrough occurred; no problem--would have been same loss as Acrodisc

- Two successful runs of Bt2 on samples 4 and 8 using method as stated in SOW.

Solution- 1. Remove Acrodisc for ethanol rinse
2. Weight reduction to 2.5 g
3.0.3 g of washed cellulose plug with appropriate blank data

The lab is allowed to use option 3 for the 6 red soils. It was suggested to "wet" preplug with several drops of extracting agent to prevent pressure head created between the polyester and soils (Cliff Jones - ERC).

Change CEC method page 3-52 step 2: change 45 ml - 35 ml to allow for complete extract with NH_4Cl or NH_4OAc

b. Detection Limit Issue

Problem - Monthly determination of IDL's by present methods causes stoppage of routine analyses and unnecessary methods delays for laboratory. Thus some IDL determinations must be made that are not associated with routine analyses.

Solution- IDL determinations should be made every three batches instead of monthly. Thus the IDL's for batch 1 and 2 should be the original IDL's used for the initial IDL determination for this contract sample analysis. IDL's for Batch 3 should be based upon blanks or low level standards from Batch 1,2, and 3. Idl's for batch 4 should be based on blanks or low level standards from batch 2,3, and 4. This resolution will cause minor changes in LEVIS. Primarily, the IDL form will be based on a batch basis instead of the present monthly basis.

c. The pH and detection limit data had no major problems based upon visual analysis.

All other data will be assessed via modem transfer to EMSL-LV and on a follow-up audit.

3. LEVIS Issues

- A spike method problem was identified through LEVIS. The laboratory was diluting first, then spiking, instead of the opposite as required. They will correct this problem.
- A system update was made to the report files and a test of LEVIS communication to EMSL-LV was successfully made.
- A 10,000 ppm spike solution was used which LEVIS could not accept because only 4 digits were allowed. A note was made in the comment file identifying the true concentration (i.e., report 1000 but add 10-fold dilution in appropriate column).

4. Sampling Scheduling

Sample shipment was discussed with the laboratory owner stating that EMSL planed on having all batches shipped to the laboratories by March 1, 1989. In addition discussions were held on the official start date of the batches the lab had receive, which are as follows:

Batch	Actual Receipt Date	Official Start Date
1	10/18/88	11/11/88
2	11/07/88	11/18/88
3	11/25/88	11/25/88

AUDIT REPORT FOR LABORATORY 2

Date of Audit: January 24-25, 1989

Participants: M. Papp, G. Byers, B. Schumacher, R. Slagle - Lockheed-ESC
L. Blume - Environmental Protection Agency

Introduction:

The purpose of this report is to document the issues raised on a recent audit of Laboratory 2 which took place on January 24-25, 1989. The purpose of this audit was to:

- assure methods and operations as stated in each of the contracts is being implemented as specified;
- to assess the quality of existing data;
- to follow-up on issues raised at past audits;
- to discuss the process used to evaluate data packages;
- to answer any miscellaneous questions concerning these contracts.

The tentative agenda that was followed for this audit was:

8:00-9:00 am	Introductory Discussions
9:00-10:30 am	Audit team caucus to evaluate the following requested information
	-Control Charts
	QCAS
	QCCS
	DL-QCCS
	- Detection Limit Raw Data
	- Total S,C, and N data for batches 1-3
	- Batch 30102, 30106, 30109 routine data
10:30-11:00 am	Debriefing to laboratory personnel on data review findings
11:00-12:00 am	Presentation to Lab On:
	- Reanalysis Template
	- Soil-chemistry Relationships
	- Control charts of Blind Samples Across all Laboratories
	- True value QCCS for particle size analysis
12:00-1:15 pm	Lunch
1:30-2:30 pm	Visit facility
2:45-5:00 pm	Laboratory tour
5:00-7:00 pm	Debriefing of audit team findings, and discussion.

The major issues and resolutions were the following:

a. Control Charts

The requested control charts were reviewed. In general, the charts were acceptable but were lacking data from batch's 30106 and 30109 which at that time were not formally submitted. And select parameters such as pH and PSA were not charted for the DL-QCCS and the QCAS. We also discussed and emphasized use of these charts by the lab manager and accessibility to technicians. This discussion was concluded by requesting formal submission of these charts to EMSL-LV after completion of the first three batches of data.

b. PSA

The silt data was consistently below the accuracy windows and the VFS was usually high. This occurrence was observed in all data submitted to date for this contract and was also observed in data from the interlaboratory comparison study. We recommended the following corrective action steps in priority order:

1. Place a 300 or 325 mesh sieve at the base of the sand fraction sieves. In this manner remnant clay or silt size material would not contribute to the VFS fraction, and the resulting silt fractions determined by difference should not be offset low.
2. Reanalysis of affected batches.
3. Run QCAS without filter candle.
4. Cross check quantitation method by using hydrometer for the QCAS sample.
5. Flow chart the individual steps of the method as interpreted by lab and compare this to other laboratories.

It seems that our first recommendation may have solved the problem based on data received after completion of the audit.

c. Moisture Content

The precision of the MC determinations observed in the first two batches of data was outside of the acceptable range. We thoroughly reviewed the handling of the samples for this measurement. It seems the problem may have been due to a new technician and due to sample handling. We requested an improved desiccation method and more emphasis on sample handling which the laboratory had instituted for the third batch of analyses. The problems were not evident after review of the third batch of data, indicating potential resolution of the problem.

d. SO4-0, SO4-2

The select isotherm points showed accuracy problems primarily biased low for the first two batches of samples. We discussed the possibility of faulty filters and/or standard preparation techniques that may account for the problem. When we discussed this problem with the technicians we observed a grade "A" pipette was not being used for the 2 ppm standard. Also we were told that a new technician prepared only the SO4-2 and SO4-0 standards while the more experienced technician prepared all others. We recommended corrective action of the identified problems followed by reanalysis of the affected batches.

e. CEC Blanks

The mean reagent blank value for CEC_CL was above the required level for the first two batches analyzed. More extensive washing procedures were applied to the pulp washing of the third batch of samples which seems to have solved the problem after evaluation of preliminary data.

f. WAL facility

The WAL facility is responsible for all ICP analyses from this contract. Most of the problems identified from the pre-award audit were rectified. The data generated by WAL has been in very good shape with no reanalyses requested. The only problem identified was some older stock standards from 1986 that were stored on a counter adjacent to the ICP. We were advised these were not being used, although we did recommend getting rid of them.

g. Total S, C, and N

The laboratory had received three batches of samples at the time of our audit visit. We were able to retrieve preliminary data from the first batch of samples, please note this was before the laboratory manager had reviewed this data. We identified the following problems:

- S_TOT spike recovery slightly above 110% (110.31%)
- reagent blank high (most likely an entry error)
- they ran one less QCCS sample
- relationships
  - C_TOT>N_TOT: one sample of 25 out
  - C_TOT/S_TOT: seven samples of 25 out
- a laboratory duplicate sample and matrix spike sample was not run with the first batch for C and N

In general, the data looked quite good for the first pass. During the laboratory tour, we emphasized that the matrix spike should be placed at the base of the combustion cell instead of the top to identify incomplete combustion, if it exists.

Overall, the audit team felt operations at laboratory were going well and as expected. Our primary concern was based on the isotherm and particle size analysis problems, although upon completion of the audit, we felt we had made much progress in solving these problems.

AUDIT REPORT FOR LABORATORY 2

Date of Audit: May 2-3, 1989

Participants:
B. Schumacher and M. Papp - Lockheed-ESC
L. Blume - United States Environmental Protection Agency
P. Shaffer - NSI Technology Services Corporation

Report: 5/2/89

: received from laboratory formal submission of CNS batches 30119, 30120, and 30121
: informed laboratory of acceptance of Batch 30116 for total CNS
: discussions were held concerning C:N and C:S ratios

- three potential reasons for failure of ratios:
    - a) wrong expectations at start of project
    - b) C_TOT values too low
    - c) N_TOT and S_TOT values too high
- it was noted that C_TOT values are in lower 1/3 of accuracy windows while N_TOT and S_TOT contents were around mean of the accuracy window therefore C_TOT is suspected to be too low
- lab stated it suspected possible contamination of samples from pyrite which was visually identified in some samples
    - not likely from our point of view because:
        - a) not mine spoil areas
        - b) horizons are oxidized Bt, Btx, Bx, and C horizons therefore most likely pyrite would already be weathered out from the pedon
- lab stated there was a possibility of N_TOT contamination due to atmospheric N in system although it should have been purged effectively
- discussed QC charts
    - N_TOT tight for accuracy and values close to mean
    - C_TOT for B and Bw horizons spread out on chart; biased low with mean; C horizons biased low with mean
    - S_TOT tight for accuracy for C horizon; Bw mean at high warning limit; B horizon had mean biased low with 9 samples out of accuracy window on the low side
- further discussions to be held tomorrow with L. Blume

: laboratory lab tour was given for both contracts

5/3/89

: M. Papp gave review of data for routine batches 30124 and 30127
: lab stated that batch 30130 would probably be ready for our initial review on Monday
: discussions were held concerning Fe and Al problem in _AO, _PYP, and _CD extracts

- reviewed QC control charts
    - _PYP extracts for LAP were running out of accuracy window high
    - _AO extracts for LAP were out of accuracy window high - even QCAS sample
    - _CD extracts for LAP were running out of accuracy window high

- lab brought up issue of temperature increases and how that influences results

    - lab noted up to a 10 or more degrees increase in temperature in shaking room between start and finish of extraction procedure
    - also have increase in ambient temperature between start of project and now

- lab stated it had a change in the method of operations between start and current analysis process for _CD extraction

    - previously lab would make _CD solution, weigh samples, and then extracts
    - now lab weighs samples, makes _CD solution, and extracts

- lab noted increased Fe contents with increased time of extraction

- lab stated it is running reanalysis of batch 30124 for Fe and Al with shaking room door open to prevent or at least help eliminate the drastic temperature rise over time

Problem Resolutions:

CNS

1) do a comparative laboratory study to check reproducibility of methods and results

a) Laboratory 3 will do a batch of samples for total C, N, and S following the contractual methods used at Laboratory 2
b) P. Shaffer will find a lab to do total C, N, and S analyses
    - preferably M. David for S_TOT and T. Strickland for N_TOT and C_TOT
    - no particular method was stated
c) Laboratory 2 will determine total C and N using coulometric and Kjeldahl methods, respectively

- Laboratory 2 will send 1 aliquot of ground soil samples to Laboratory 4 and 2 aliquots to P. Shaffer for further distribution
- batches selected were batch 30114 and as an alternative 30119

2) batches with more than 6 soil chemistry relationships failing will not be called for reanalysis at this time as agreed on by all parties present pending the results of the comparative laboratory study

Fe and Al

1) will wait for results of reruns of batch 30124 and new results of batch 30130 to determine if "cooler" temperatures had an influence on results especially of the B horizon LAPs

2) lab will FAX data for batch 30130 on Friday - batch will be 6 samples short and possibly a QCCS sample short due to misplacement of samples

AUDIT REPORT FOR LABORATORY 3

Audit Date: November 9, 1988

Participants: L. Blume - United States Environmental Protection Agency
B. Schumacher, R. Slagle - Lockheed-ESC
C. Palmer - Environmental Research Center-LV

Introduction:

A laboratory audit was conducted on Wednesday November 9, 1988 of Laboratory 3. Analytical services are being provided by this laboratory to the Direct/Delayed Response Project in support of the Mid-Appalachian Soil Survey. The objectives of the audit were to:

1) Evaluate progress since the pre-award audit;
2) Examine preliminary data;
3) Discuss the implementation of LEVIS (Laboratory Evaluation and Verification Information System);
4) Discuss the use of quality control charts;
5) Expand the awareness of data user needs to the laboratory personnel.

Report

1) Progress since the pre-award audit

Approximately 50% of the parameters for the first batch of samples had been completed at the time of this audit. The laboratory was experiencing problems with the heavier clay soils clogging in the pre-plug during the analysis of cation exchange capacity and exchangeable cations. A recommendation was provided of reducing the weight of sample for these soils down to 2.5 grams. The QA officer will provide a letter of approval to substitute the sample size from 5.00 grams down to 2.50 grams for individual samples experiencing clogging problems.

2) Examination of preliminary data

A review of the data indicated that several data entry errors were occurring. For example, sample #3 for PH_002 M of the first batch had a pH reading of 4.43 on the raw data sheet but was entered as 4.35. Sample #2 for CA_CL2 was recorded as 51.7 on the raw data sheet, but had been entered as 51.4. It was noted that verification of the data entry process had not taken place and that this would be addressed.

The QCCS sample for Ca in CA_CL2 was not in mid-calibration range as requested in the protocols nor did the calibration standards span the range of concentrations in the soil extracts. The laboratory staff indicated that the quality of the results would not be affected due to the linearity of response of the ICP analysis for Ca. They noted that any inter-element interferences are not correctable if high concentration standards are used a clear standard is needed. It was felt that the instrument could correct for any inter-element problems with the present standards.

The laboratory is to provide proof of this linearity up to 100 ppm for one batch of samples for evaluation by the QA staff. All appropriate data will be included. After review of the results, a decision will be made and the laboratory notified.

A review of the QC data indicated that the QCAS was below the acceptable window for FE_PYP. The IDL's for AL_CD and FE_CD had been determined on 11/2, 11/3, and 11,7 but were recorded as being completed on 11/4.

A review of the QE sample data (blind samples) indicated an overall very good precision for the laboratory. A few blind audit samples we found to be outside of previously determined windows. An overall evaluation of the results will be undertaken once the batch is formally submitted to see if these results warrant the reanalysis of the batch for any given parameter.

3) Implementation of LEVIS

The completed LEVIS has been completed and was delivered to the laboratory on Monday, November 7. It was noted that a separate program is being developed for the organic soil batches. It is structured the same as the LEVIS for mineral soils and will be installed when the first batch of organic soils is sent.

4) Quality control charts

C. Palmer gave a presentation on control charting along with recommended charting procedures for the laboratory. The charting of the QCAS was particularly encouraged as a means of reducing between batch variability. Concern was expressed by the laboratory over the potentially large amount of effort charting could require. It was noted that computer programs exist to assist with charting tasks.

5) Meeting data user needs

The laboratory staff was provided with a short explanation of the purpose of the DDRP Mid-Appalachian soil survey and the role of soil measurements in the final interpretations. Special attention was given to the importance of high quality data to the overall success of the program.

Summary Comments and Recommendations:

The purpose of this audit was to make an early assessment of the performance of the laboratory in the analysis of routine samples and identify and correct problems at an early stage. Evaluation of results was limited to approximately 50% of the parameters from the first batch that had been sent to the laboratory.

Specific problems that were identified included the need for checks to prevent data entry errors and an evaluation of the standards in use for the analysis of CA_CL2. Additional consideration is to be given to modifying the CEC and exchangeable cation procedures as modifications to the filter pulp method have created clogging problems for certain soils.

It appears that LEVIS will be successfully implemented in this laboratory. The importance of control charting was introduced to the laboratory as well as suggestions for implementing charting for certain key quality control samples.

In general terms, the audit team was pleased at the progress of the laboratory with the new soil samples, their cooperative attitude in working with the DDRP QA staff, and their commitment to high quality data.

AUDIT REPORT FOR LABORATORY 3

Date of Audit: March 12, 1989

Participants: B. Schumacher, G. Byers, R. Slagle, Lockheed-ESC

Report:

The audit schedule was to spend the major part of the day with the manager of the Chemistry Division, and the supervisor of the Environmental Chemistry subdivision, discussing issues of concern. The remainder of the time would be spent on an audit tour of the laboratory and closing discussions.

The meeting commenced at 9:00 a.m. with an introduction by B. Schumacher of the purposes and goals to be accomplished for the audit. G. Byers then gave an overview of the various procedures used at Lockheed to assess the QA/QC requirements prior to officially accepting the data. His presentation included a detailed discussion using overheads of the templates used in assessing the data for acceptance and the procedures involved in reanalysis, a detailed discussion of the sample design for the quality assurance samples used in the DDRP on a batch basis, and the internal consistency procedures. B. Schumacher then used a batch of soil analytical results (batch 30114) as an example for the detailed stepwise procedures used in evaluating soil data on a batch basis.

Considerable discussion followed regarding problems and issues related to Laboratory 3 data and the specific analytical and reporting issues for data having been assigned minor and major flags. Issues such as reanalysis of the parameter PH_H2O, assembling the windows for the QCAS sample (Sample #15) for the organic soil batches, instrumentation issues and other details were discussed. A copy of the handwritten report summarizing the reanalysis requests for batch 30114, as well as copies of the previous reports where flags occurred, were provided to the laboratory manager. In addition, B. Schumacher received all initial IDL data for the Lockheed-ESC data files and verification of the 100 ppm standard required by the laboratory for CACL2 (see previous audit report).

G. Byers was escorted by the environmental chemistry supervisor on a laboratory tour. of the facilities used for the DDRP soils. Detailed discussion took place regarding the various procedures and instrumentation used by the laboratory in the soil analyses.

R. Slagle worked with the computer technician on the installation of a version of the computer program for the organic soil analysis reporting system using the LEVIS data entry system. Any problems involved with LEVIS were discussed. In addition, R. Slagle archived the laboratories soils data bases, removed an expanded memory board, and updated LEVIS for the mineral soils.

After lunch, B. Schumacher, R. Slagle and the laboratory manager joined G. Byers and the laboratory supervisor and toured the soil sample entry room, soil sample preparation area, and soil sample storage room in the basement. Discussions continued as the laboratory representatives completed the tour of the soil analysis section and other facilities of interest. The group then met for a final summary of the audit.

Overall, the operations and soil analysis system used by laboratory 3 for the DDRP soils were very satisfactory. The laboratory has had a history from the beginning of the program of providing prompt and satisfactory data from the quality assurance aspect. The laboratory staff was encouraged to keep up the very high caliber of data analysis.

The laboratory procedures used in the soil analytical methods by the laboratory for the DDRP soils were being followed. Protocols were being met. No problems were found in the analytical phase of the soil analysis system.

The storage, handling, identification, and retrieval system for soils samples used by the laboratory were satisfactory. The organized manner and overall cleanliness of the facilities were also noted.

Overall, the performance of laboratory computer data processing facility in the use of the LEVIS reporting system was excellent. No problems were found.

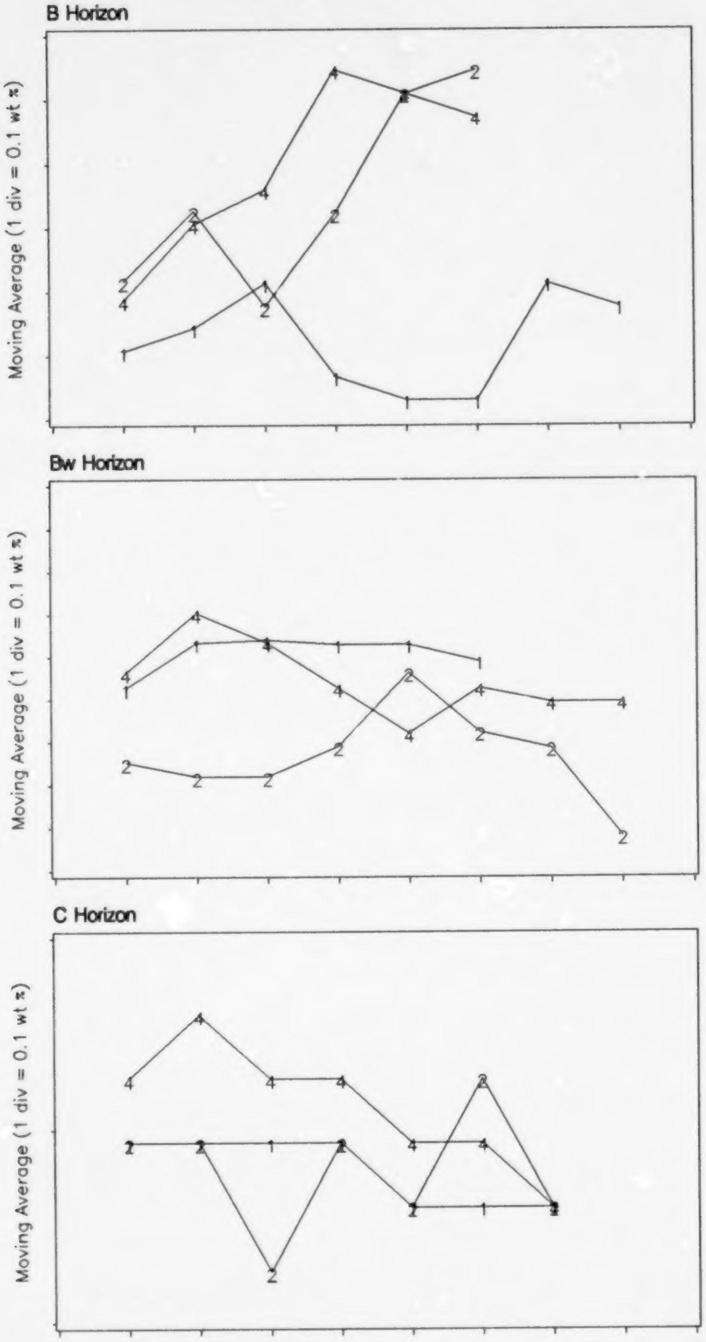
Appendix I

Plots of Moving Averages for Laboratory Audit Samples

This appendix contains plots of three-point moving averages showing laboratory trends for the MASS data collected from the B, Bw, and C horizon laboratory audit samples. Each plot depicts the temporal distributions of the moving averages in relation to the boundaries of the accuracy windows and their associated reference values. No conclusions have been made on the significance of differences seen in the plots, or which of the apparent trends may be of importance to the data users.

MOIST

Air-Dry Moisture

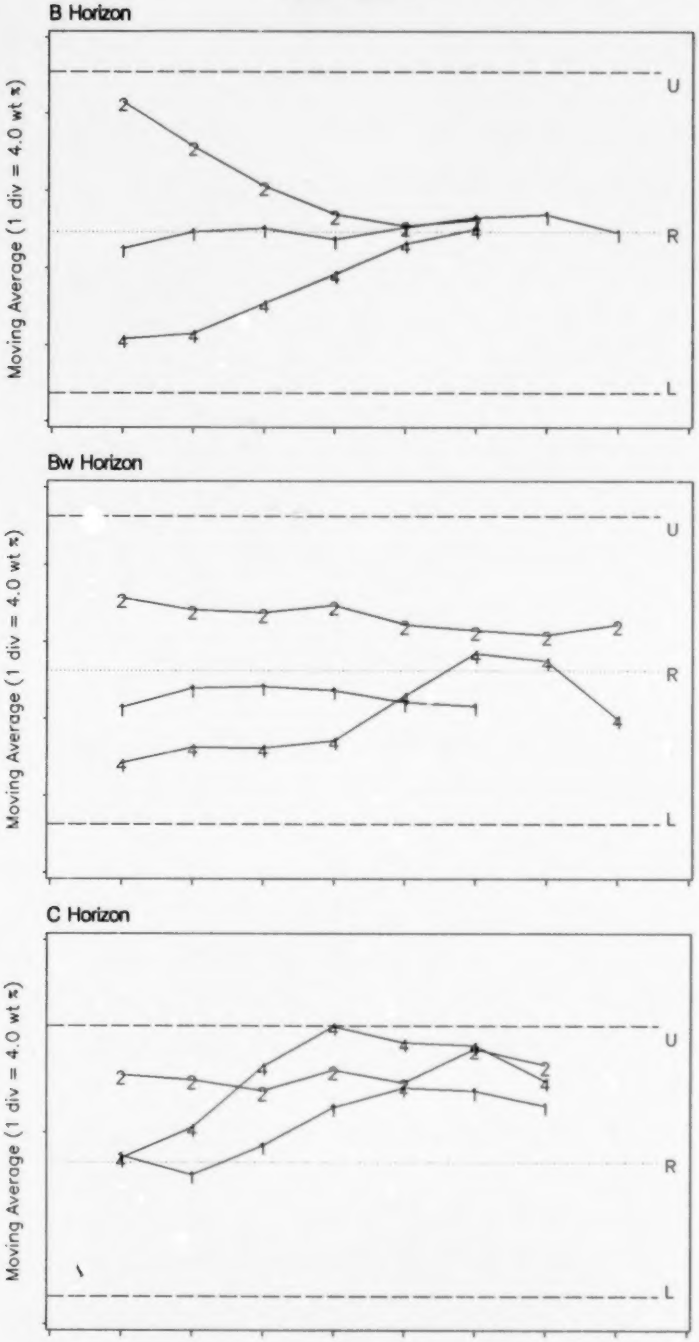


U = Upper Limit L = Lower Limit R = Reference Value

Figure I-1. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for MOIST.

SAND

Total Sand



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-2. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SAND.

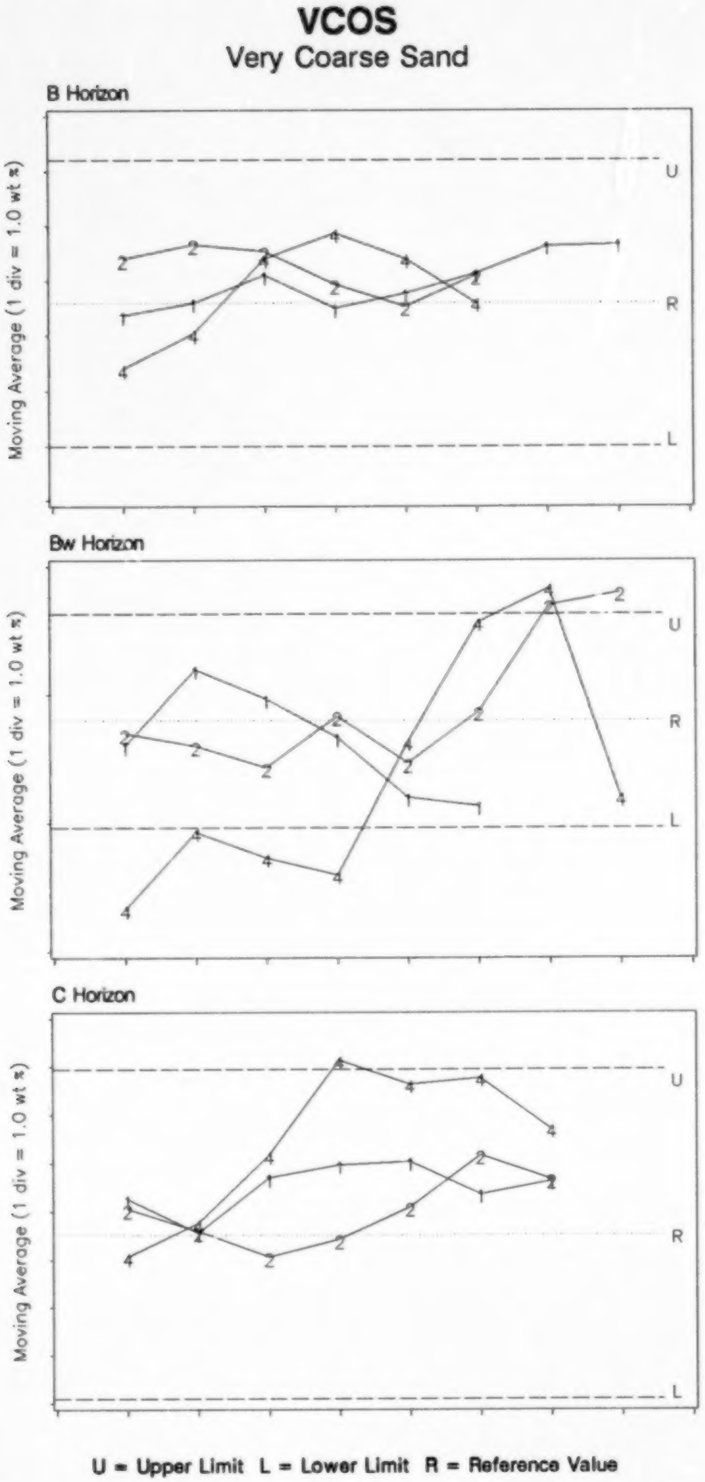


Figure I-3. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for VCOS.

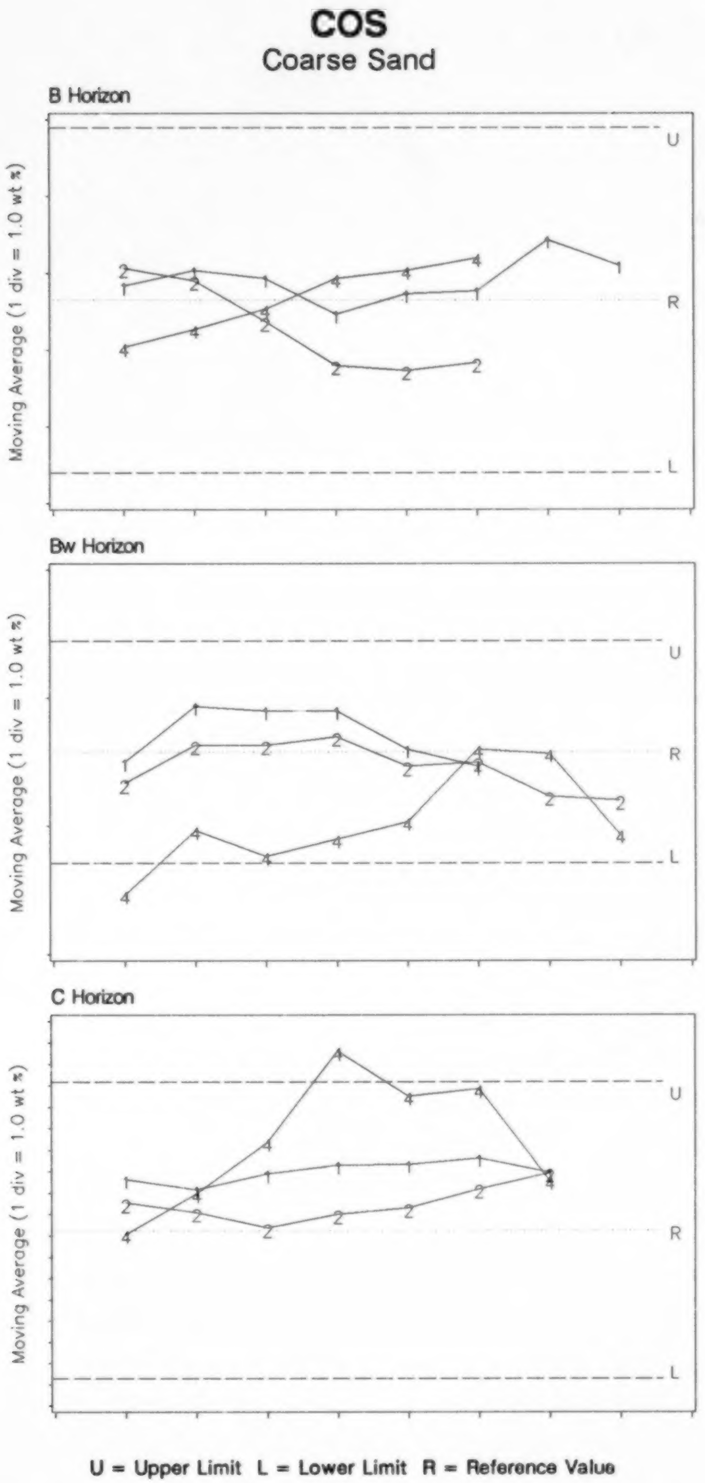
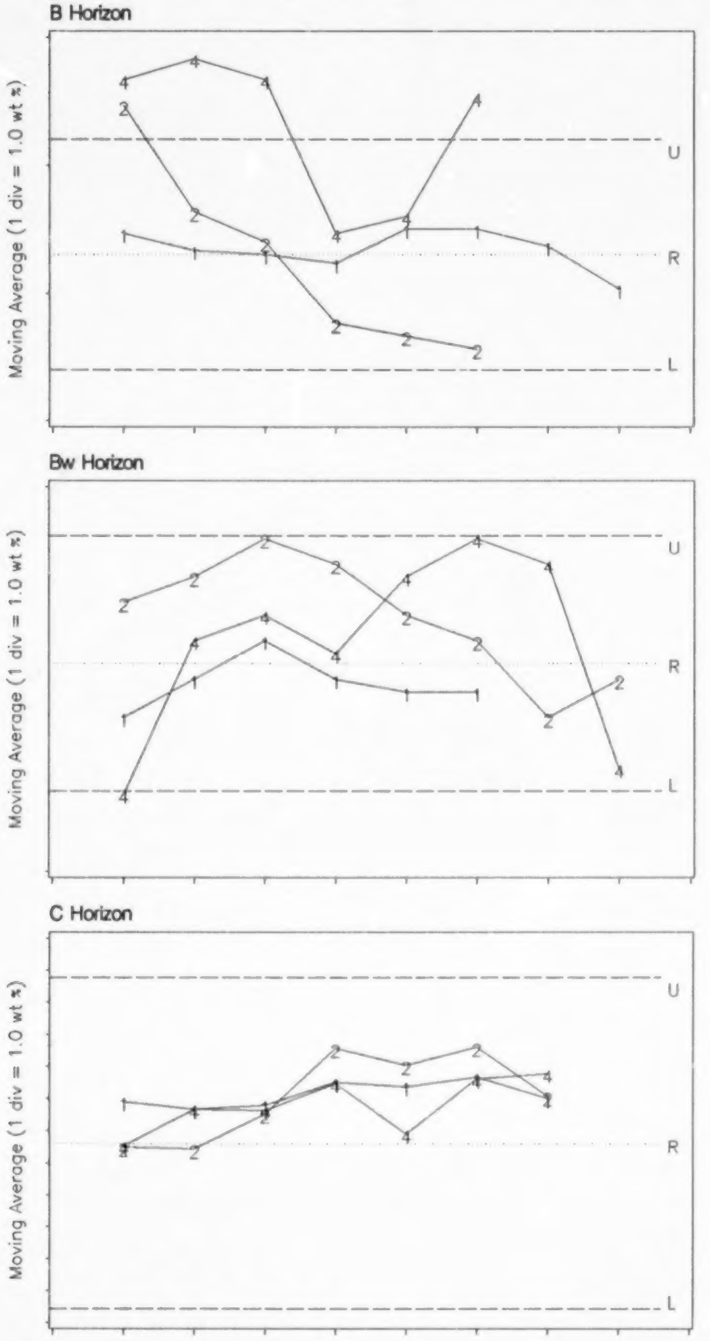


Figure I-4. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for COS.

MS
Medium Sand

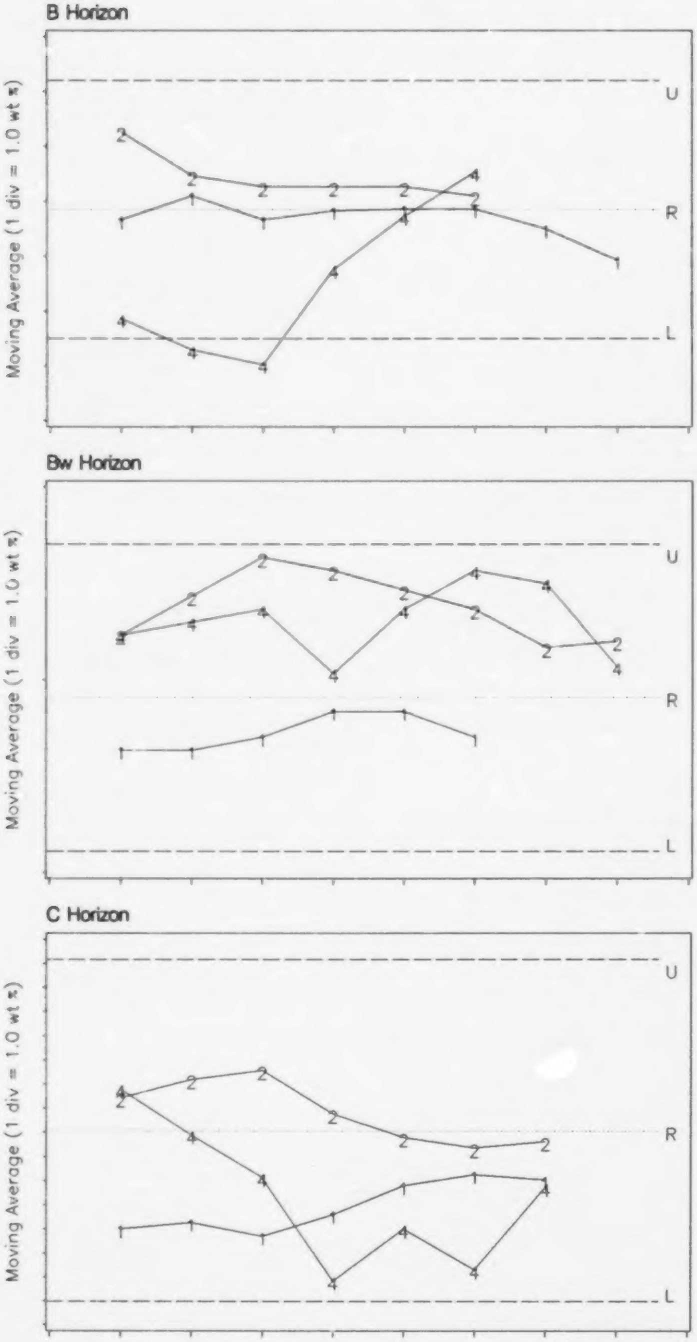


U = Upper Limit L = Lower Limit R = Reference Value

Figure I-5. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for MS.

FS

Fine Sand

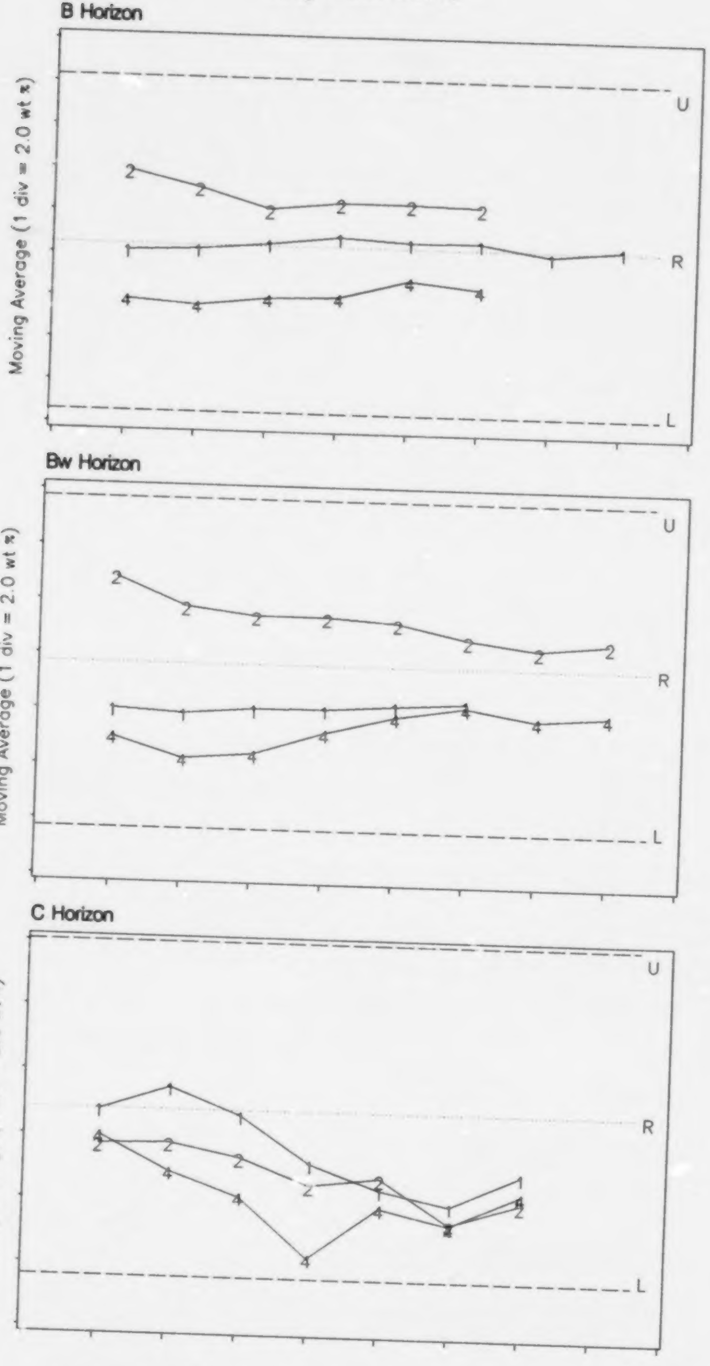


U = Upper Limit L = Lower Limit R = Reference Value

Figure I-6. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for FS.

VFS

Very Fine Sand

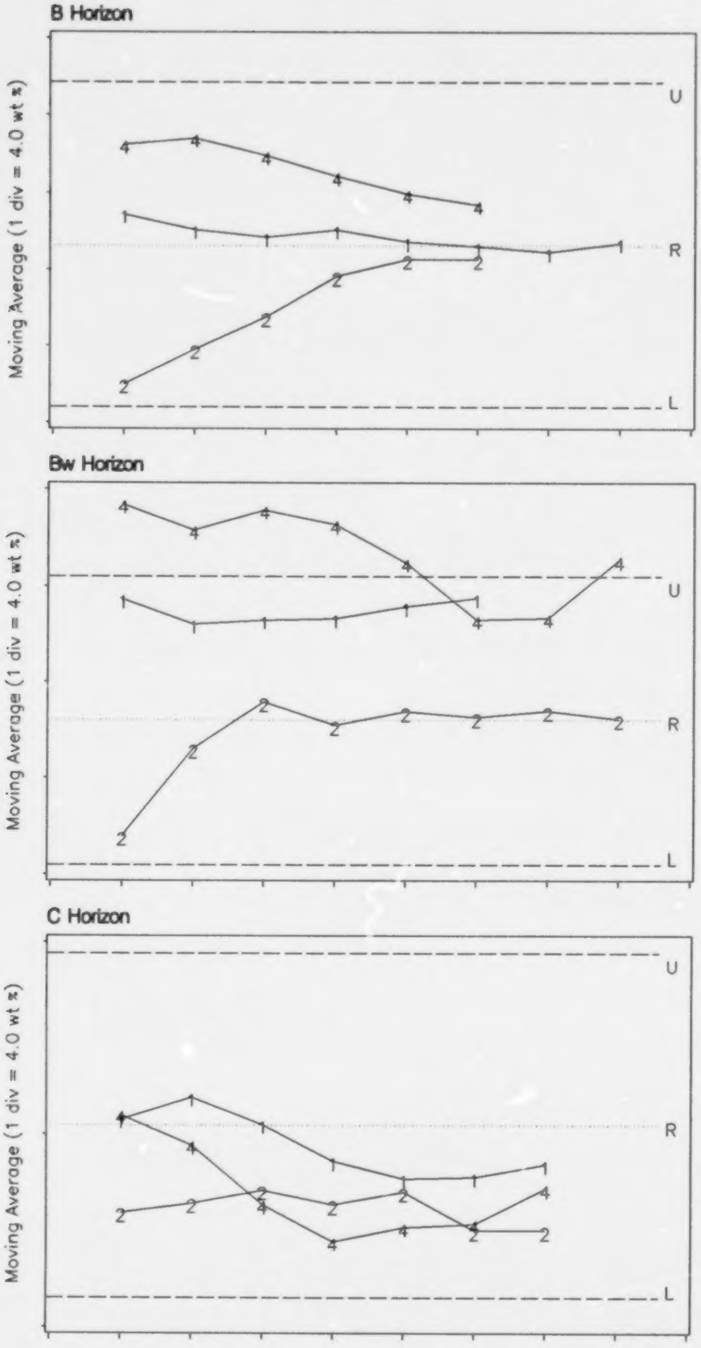


U = Upper Limit L = Lower Limit R = Reference Value

Figure I-7. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for VFS.

SILT

Total Silt

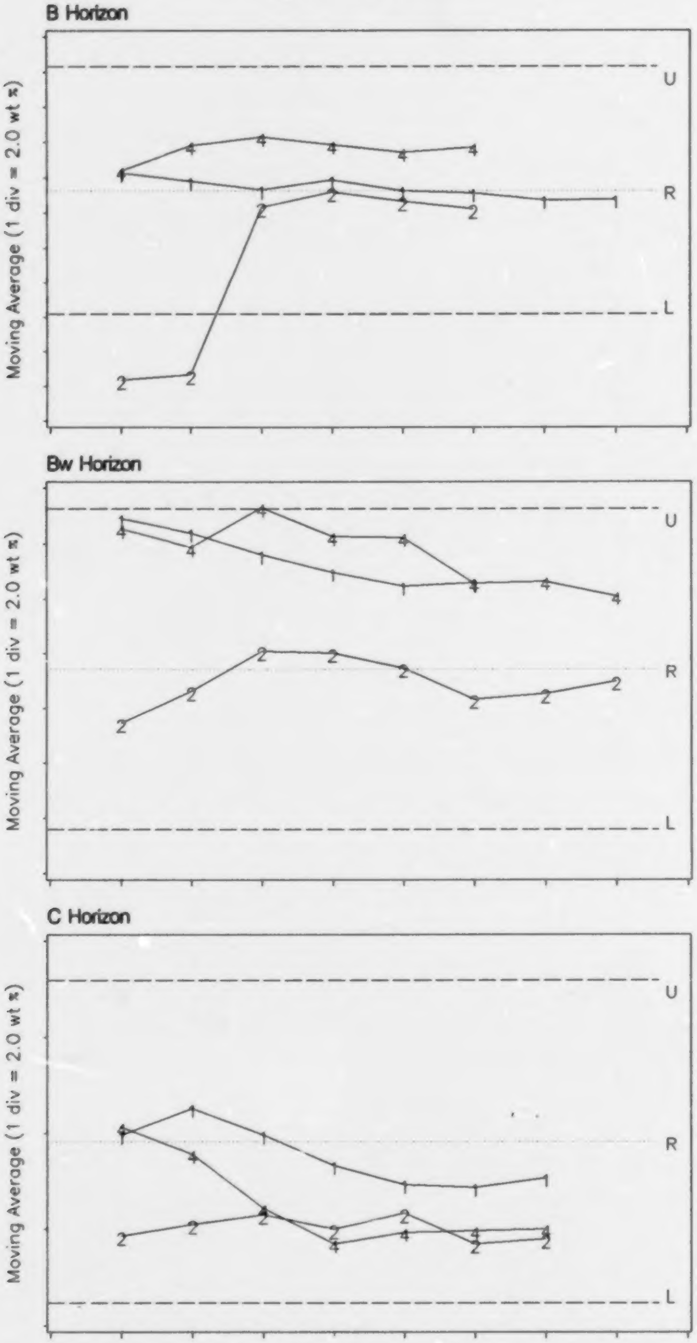


U = Upper Limit L = Lower Limit R = Reference Value

Figure I-8. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SILT.

COSI

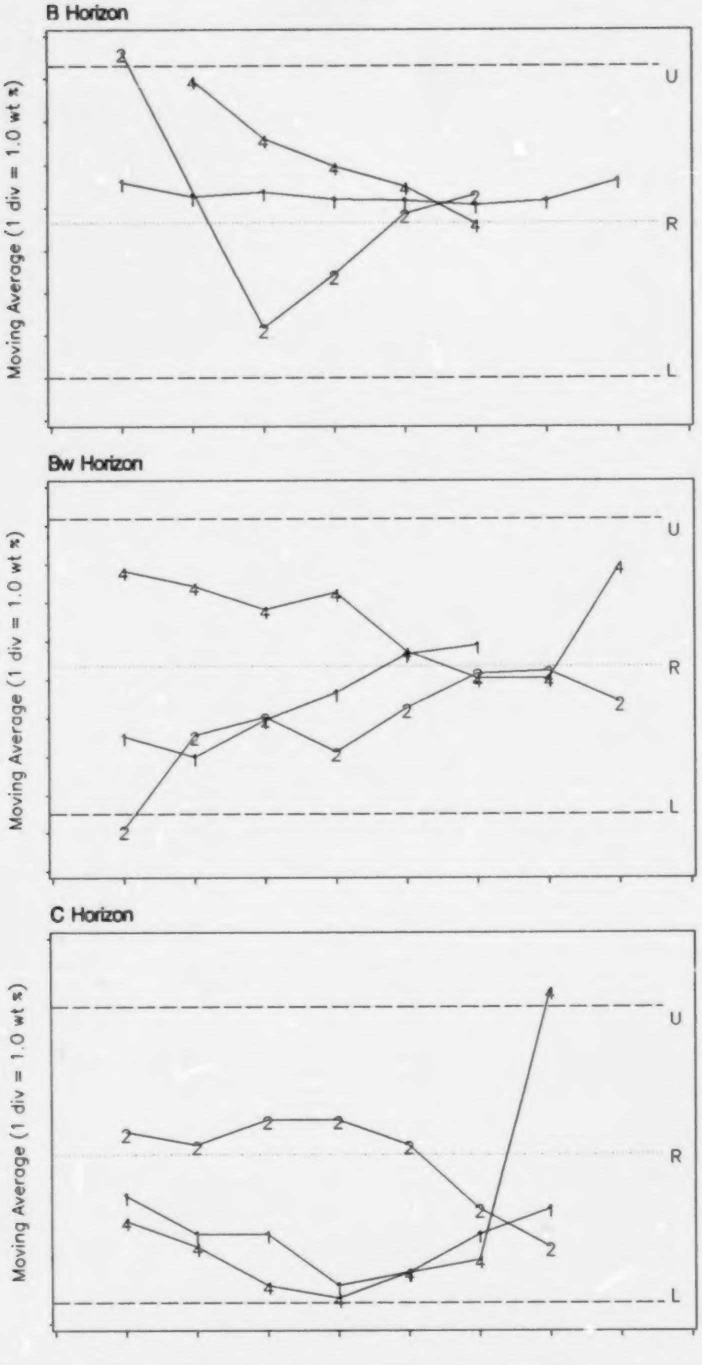
Coarse Silt



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-9. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for COSI.

FSI
Fine Silt



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-10. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for FSI.

CLAY
Total Clay

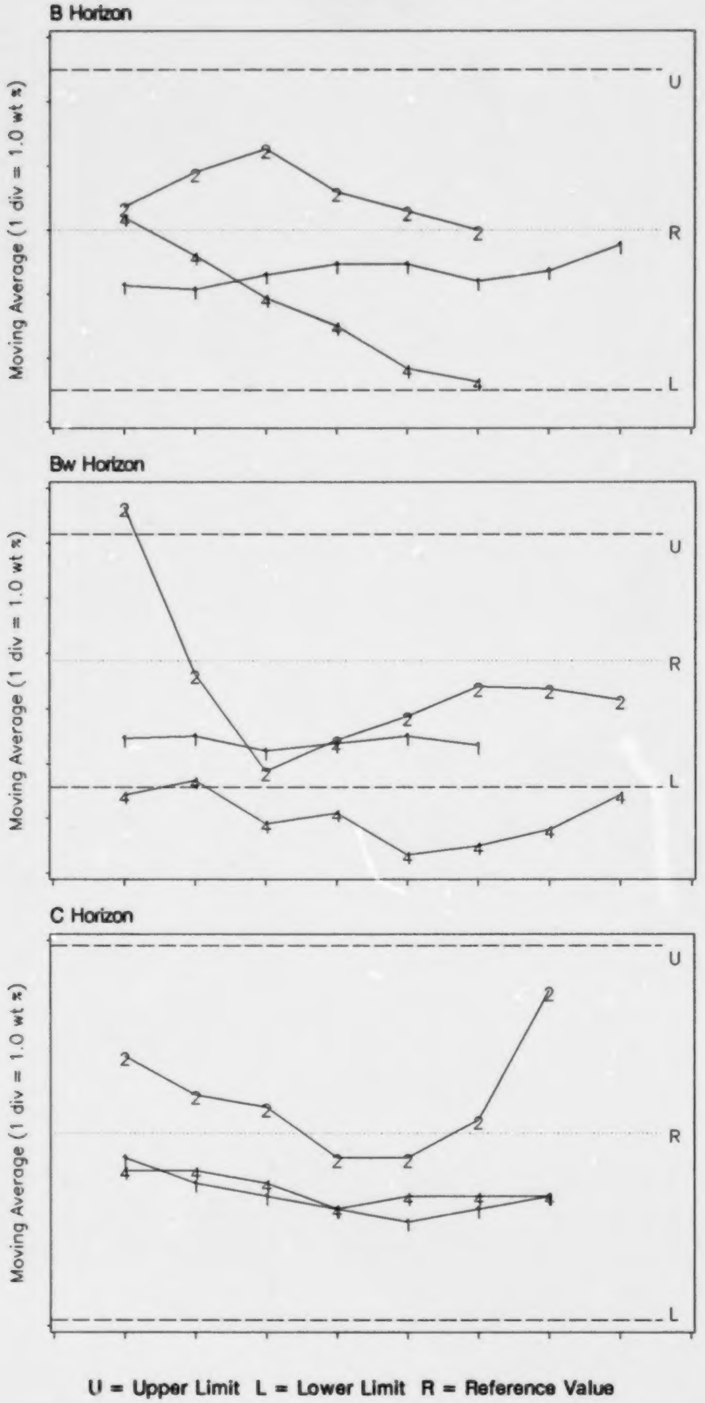
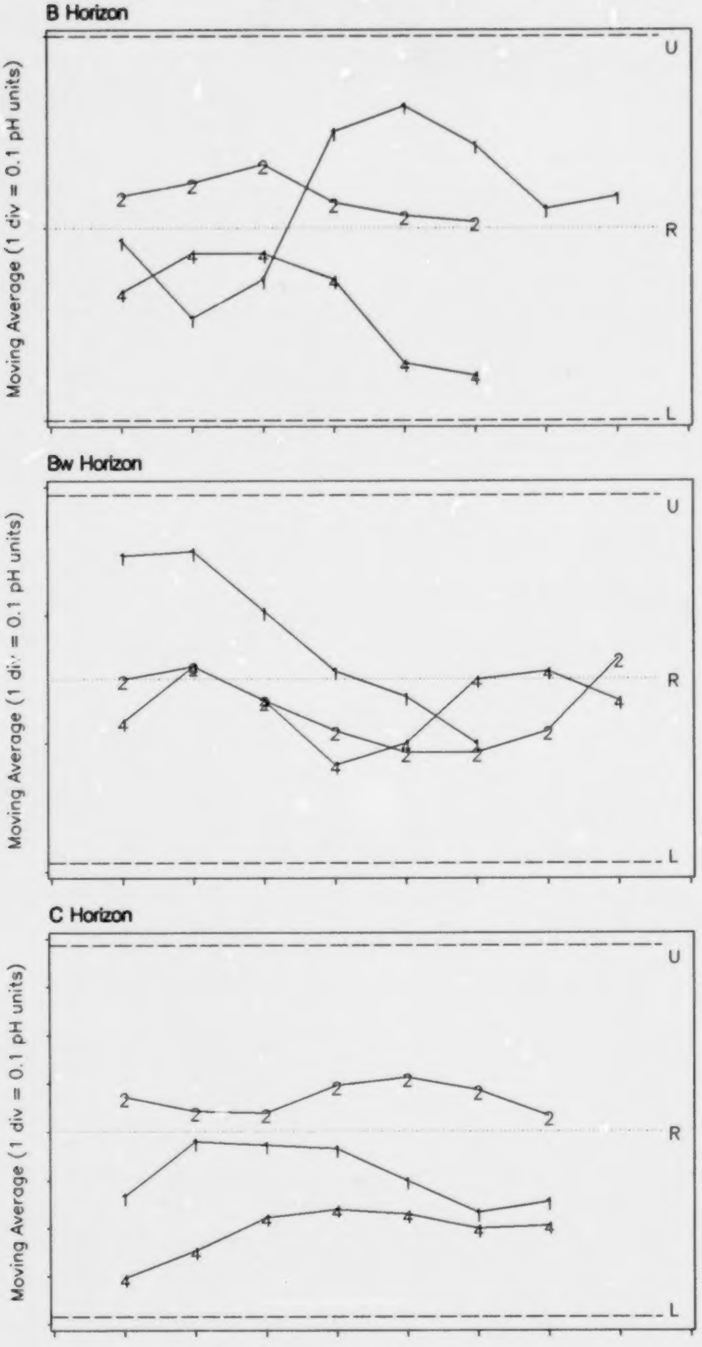


Figure I-11. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for CLAY.

PH_H20
pH in water



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-12. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for PH_H20.

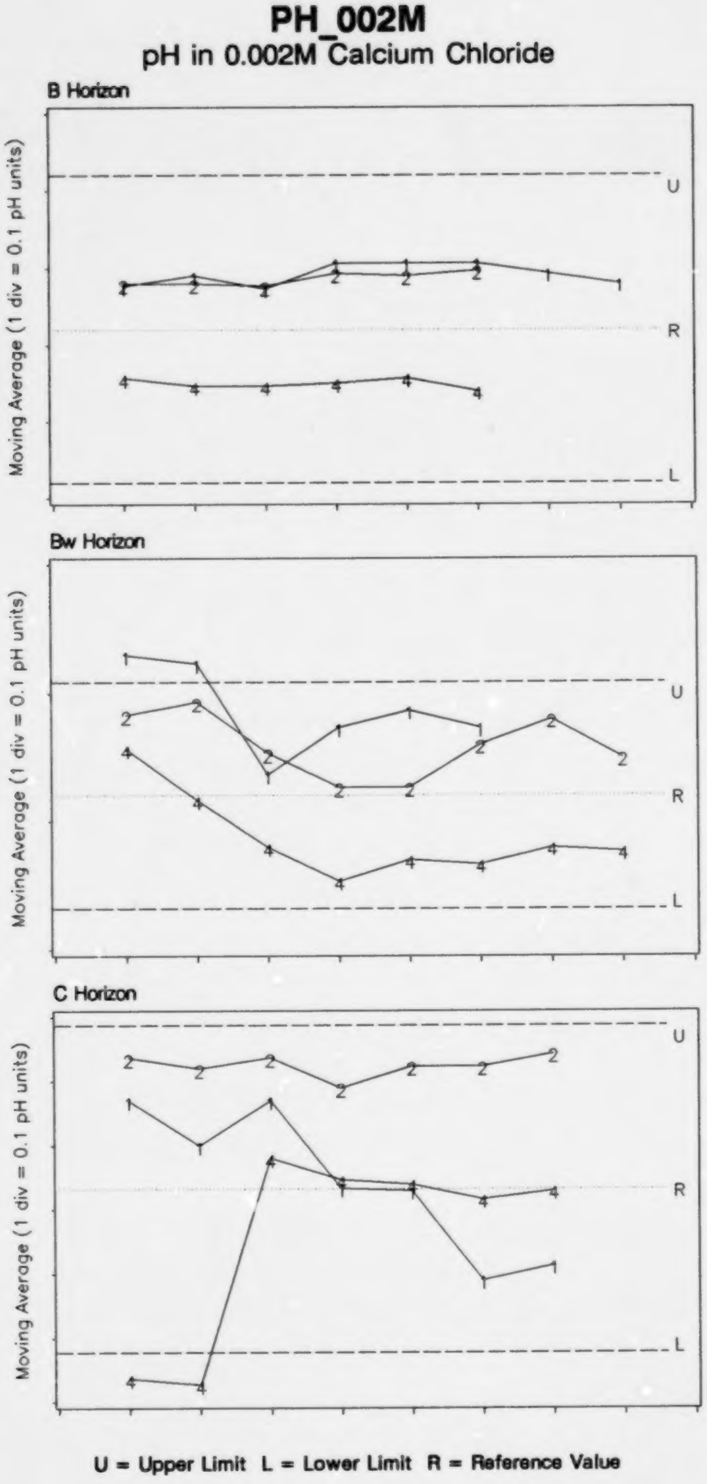


Figure I-13. **Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for PH_002M.**

PH_01M
pH in 0.01M Calcium Chloride

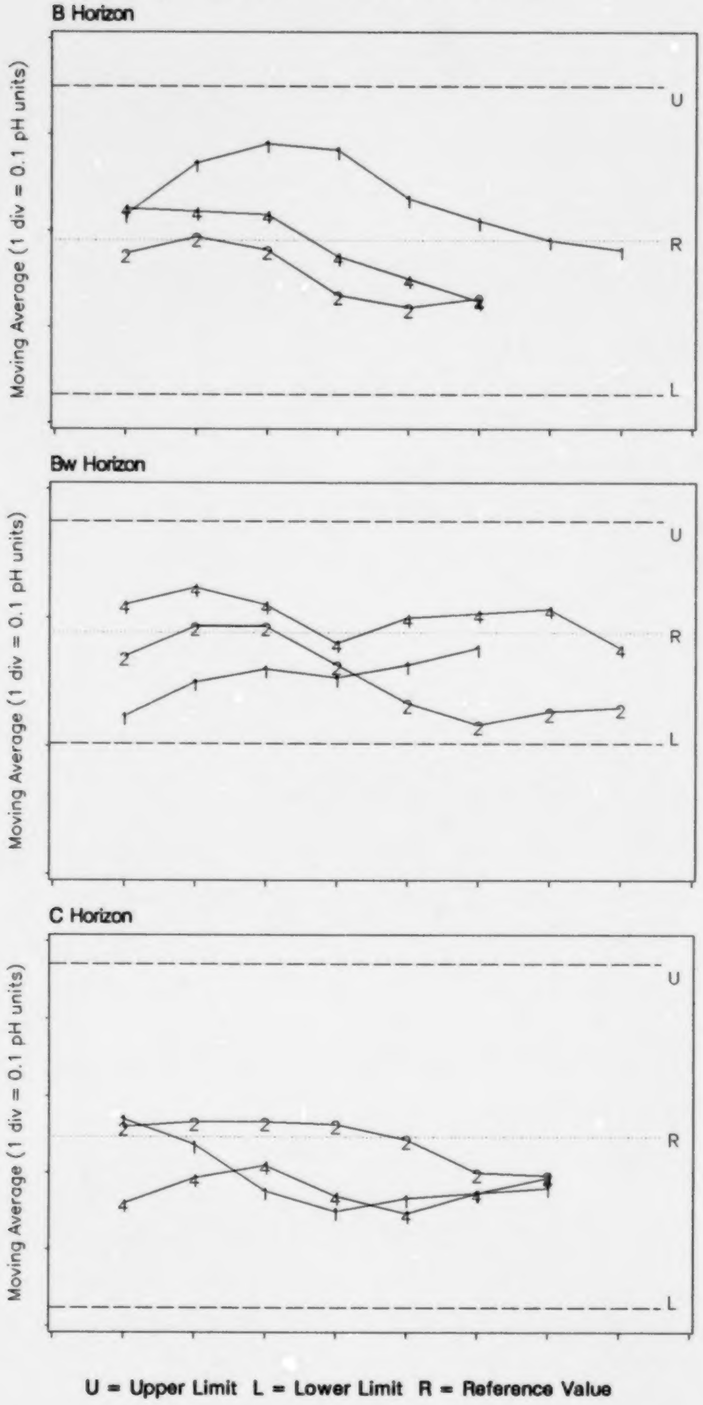
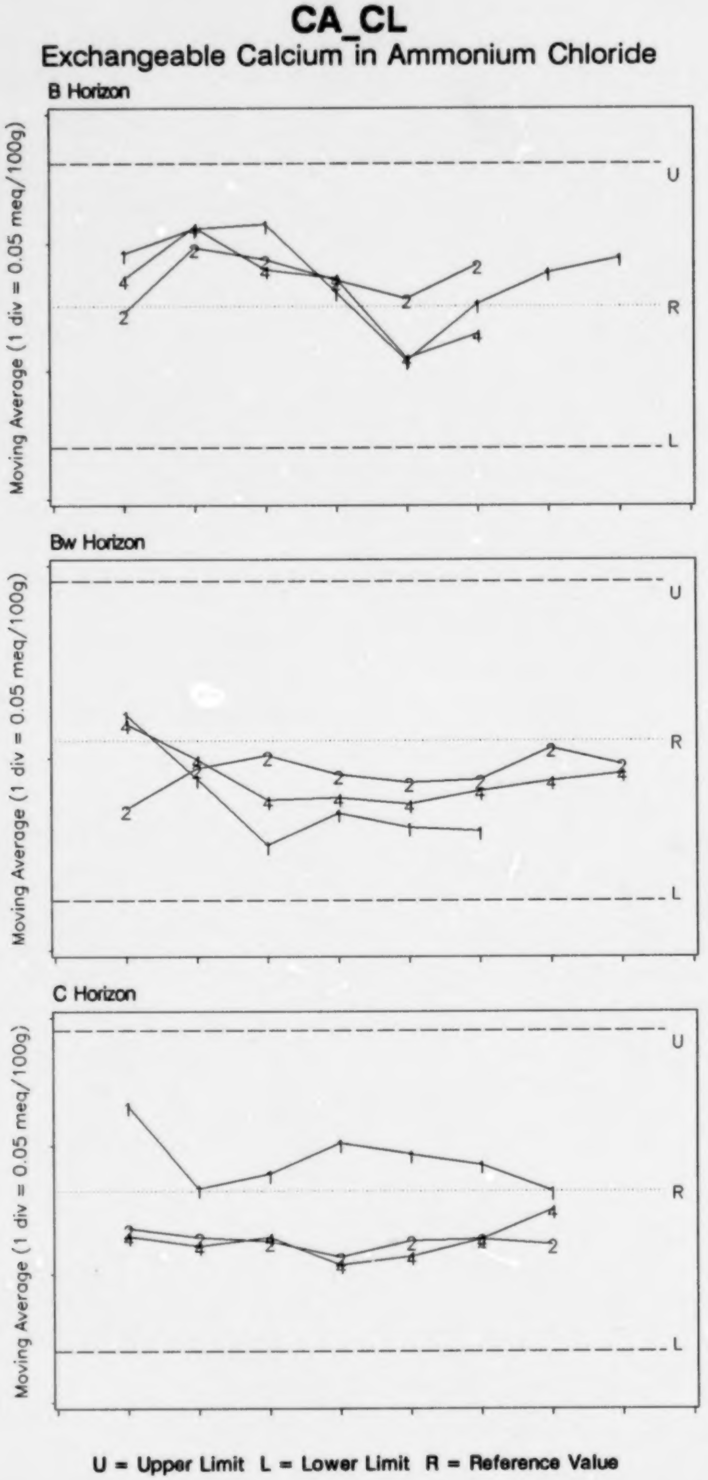


Figure I-14. **Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for PH_01M.**


CA_CL

Exchangeable Calcium in Ammonium Chloride

B Horizon

Bw Horizon

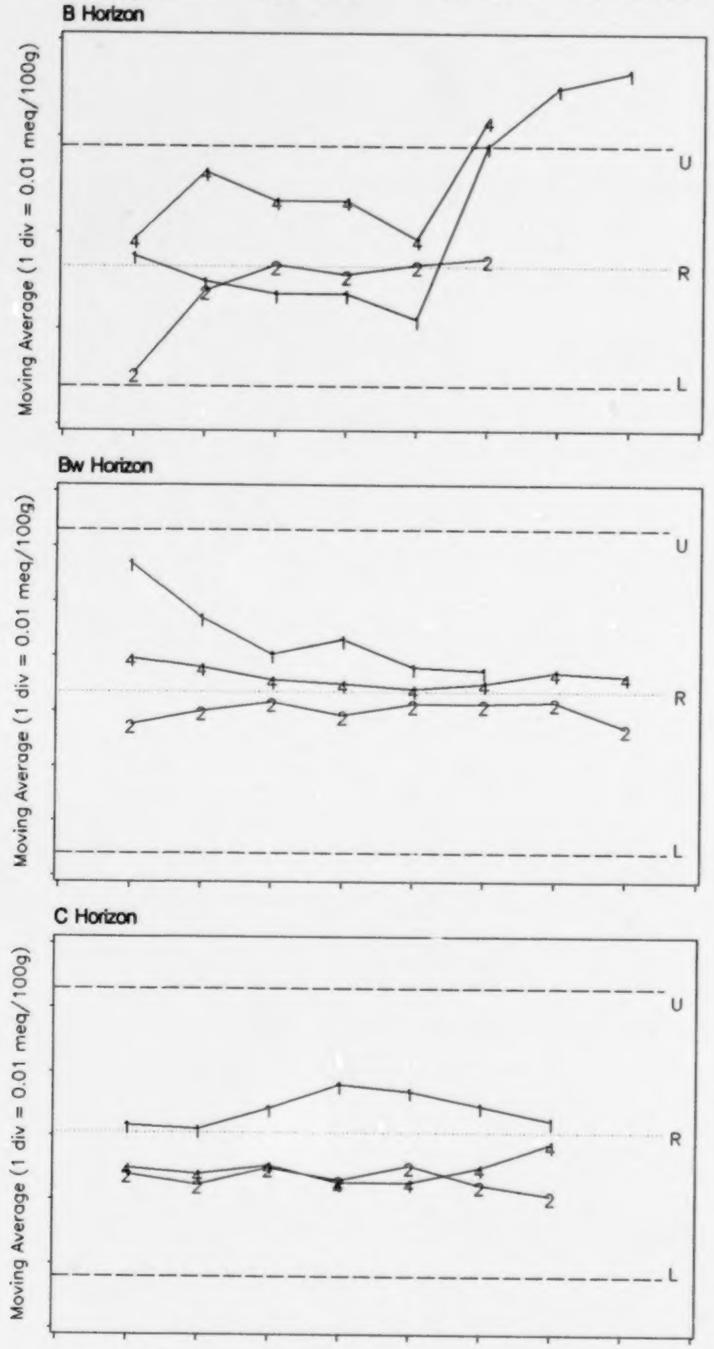
C Horizon

U = Upper Limit L = Lower Limit R = Reference Value

Figure I-15. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for CA_CL.

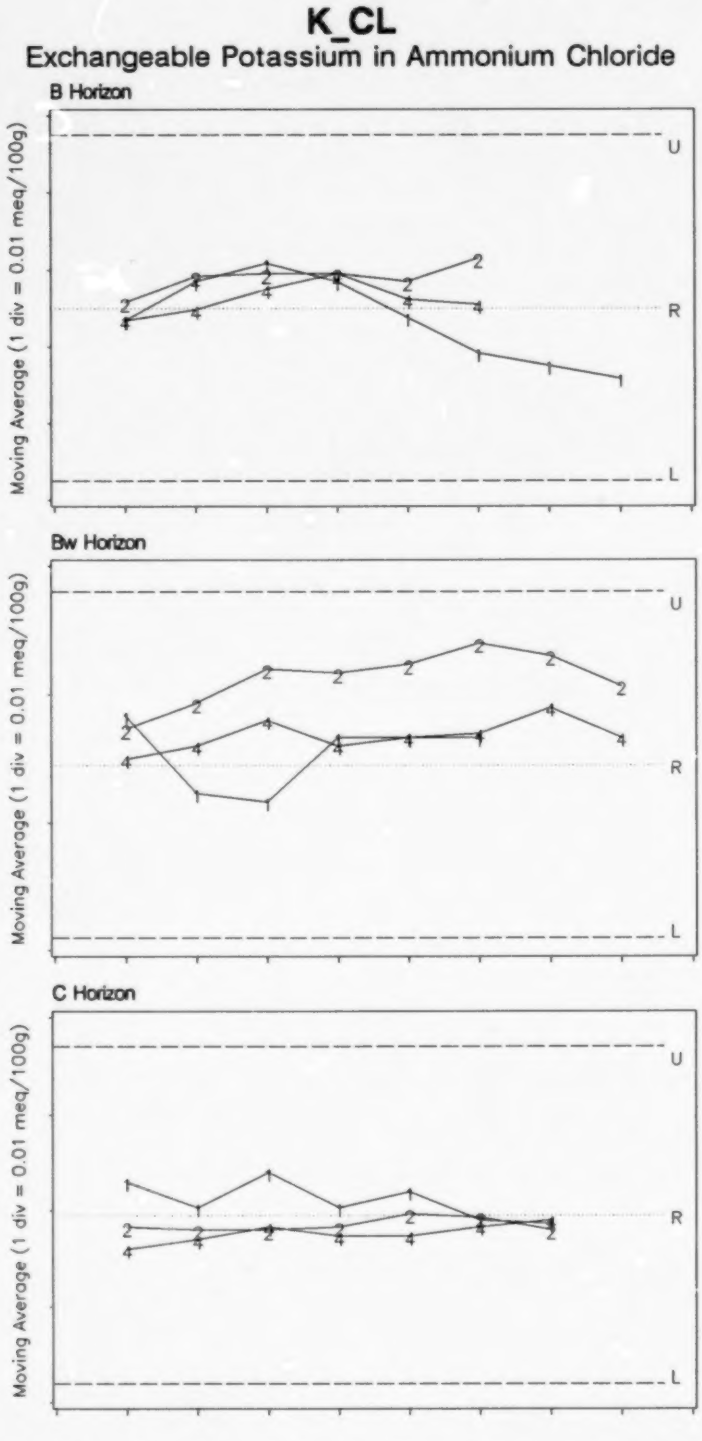
MG_CL

Exchangeable Magnesium in Ammonium Chloride



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-16. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for MG_CL.


K_CL

Exchangeable Potassium in Ammonium Chloride

B Horizon

Bw Horizon

C Horizon

U = Upper Limit L = Lower Limit R = Reference Value

Figure I-17. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for K_CL.

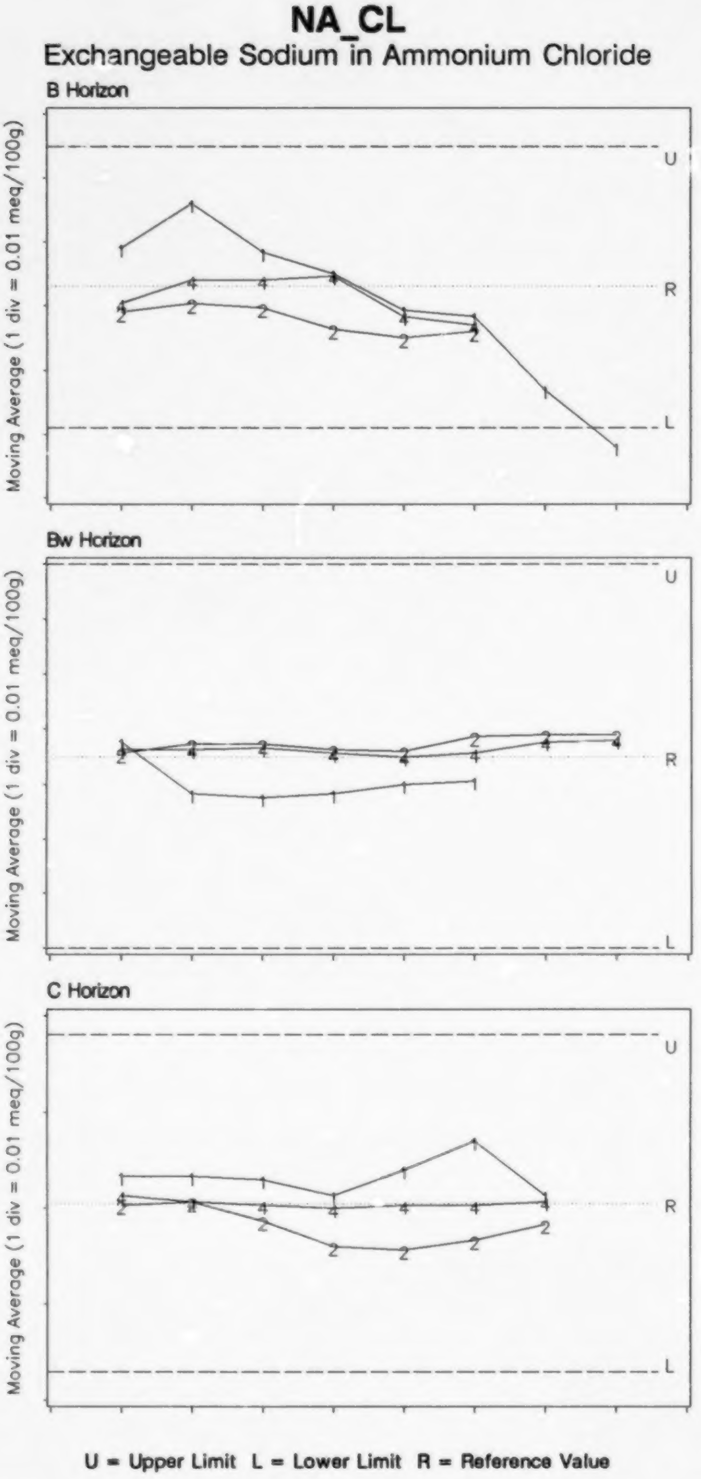
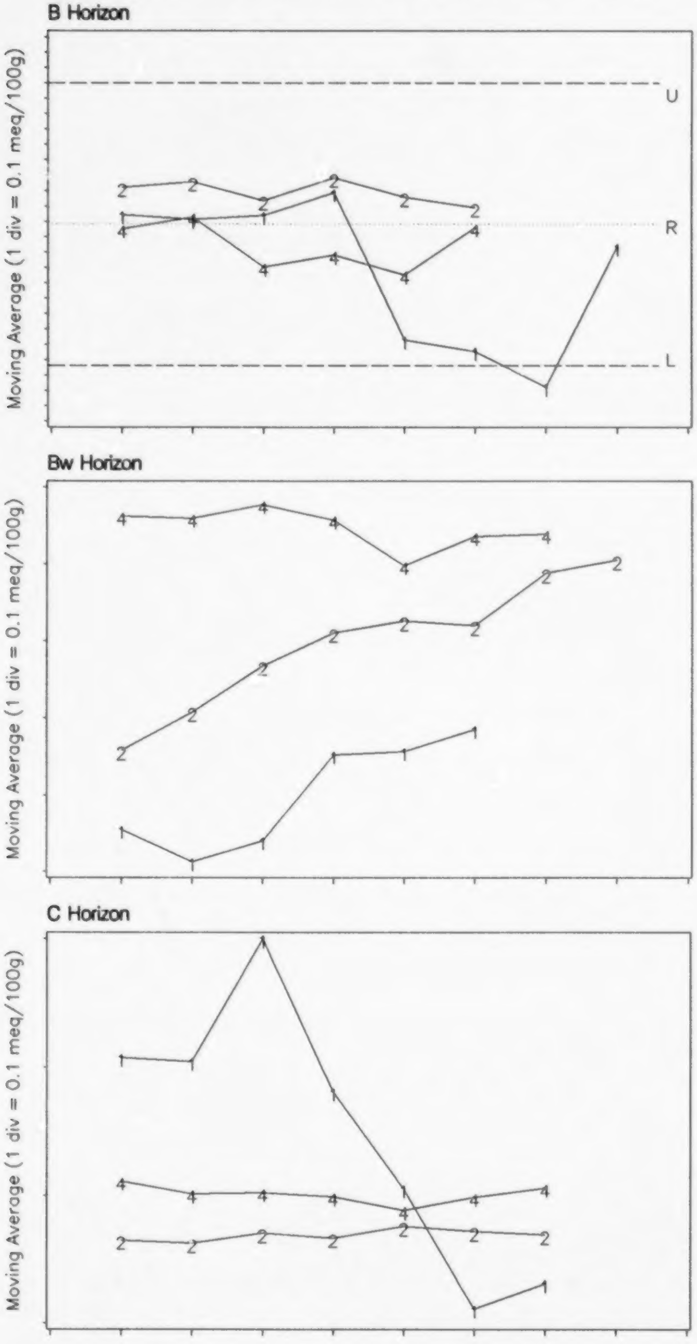


Figure I-18. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for NA_CL.

AL_CL

Exchangeable Aluminum in Ammonium Chloride

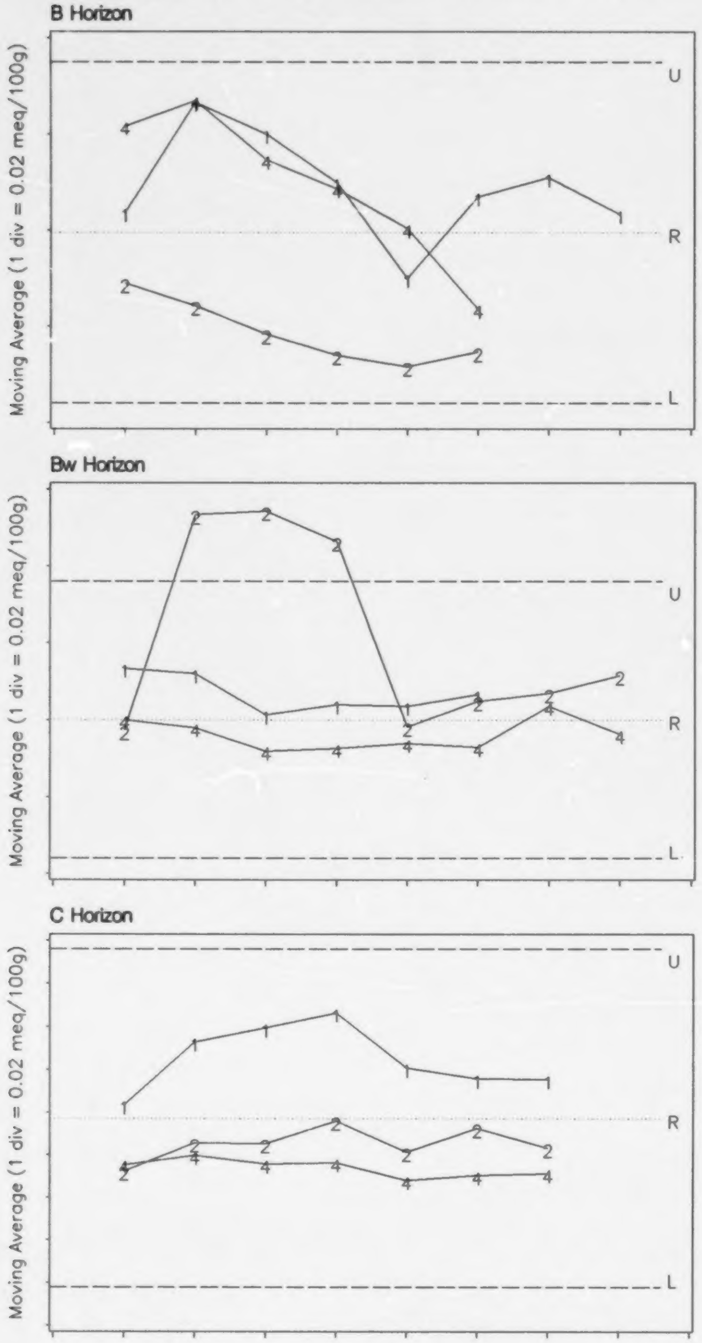


U = Upper Limit L = Lower Limit R = Reference Value

Figure I-19. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for AL_CL.

CA_OAC

Exchangeable Calcium in Ammonium Acetate



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-20. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for CA_OAC.

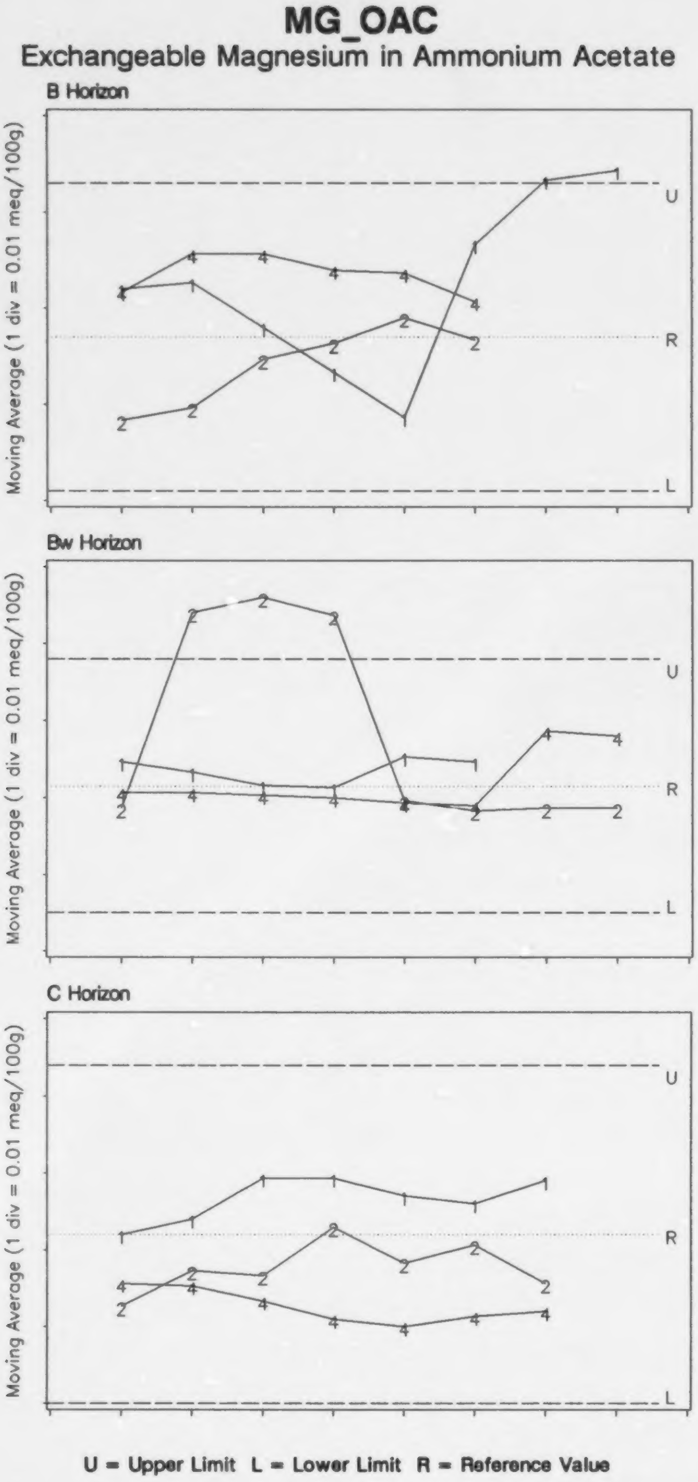


Figure I-21. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for MG_OAC.

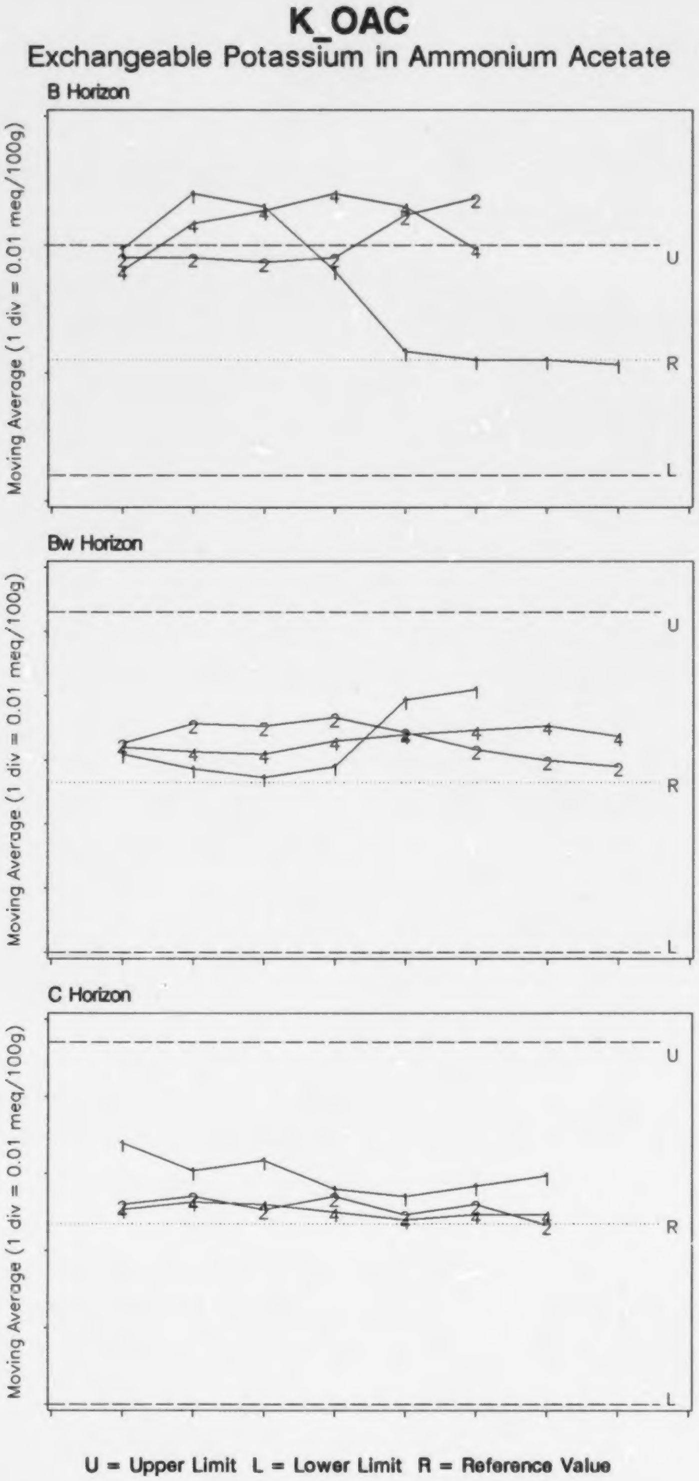


Figure I-22. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for K_OAC.

NA_OAC

Exchangeable Sodium in Ammonium Acetate

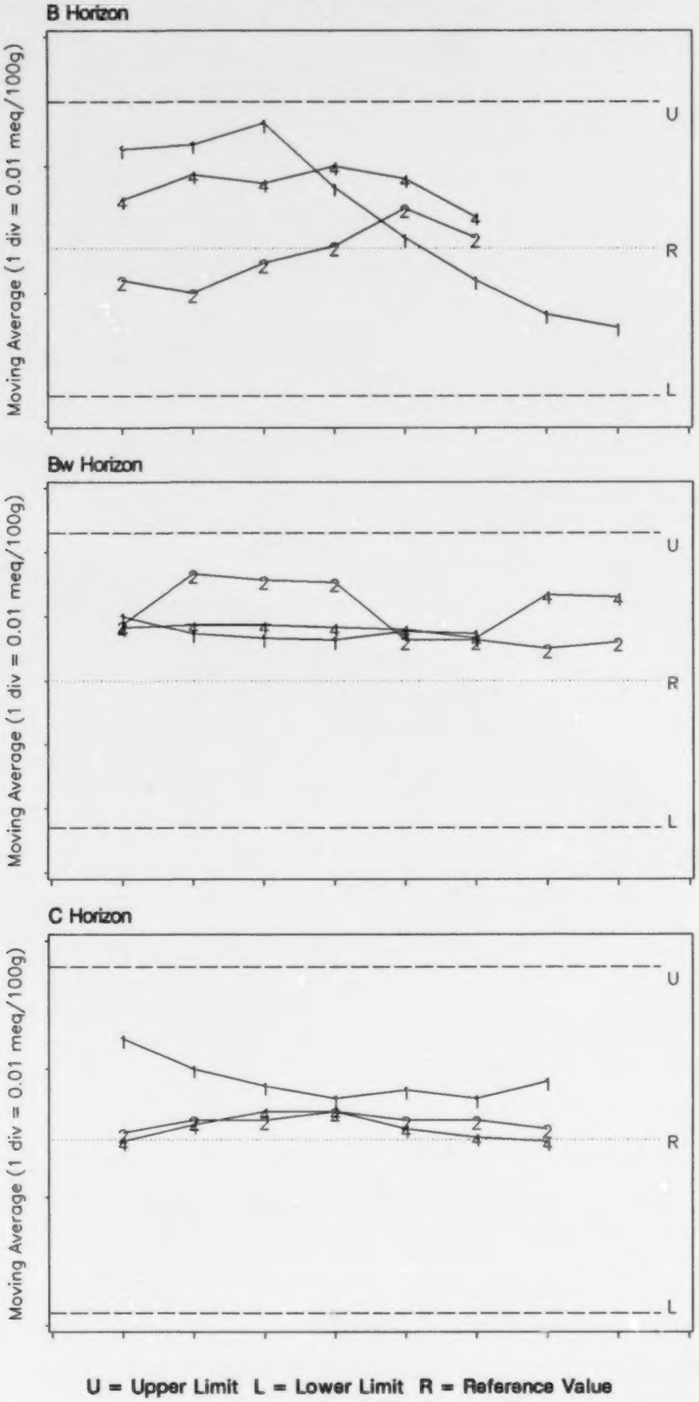


Figure I-23. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for NA_OAC.

CEC_CL

Cation Exchange Capacity by Ammonium Chloride

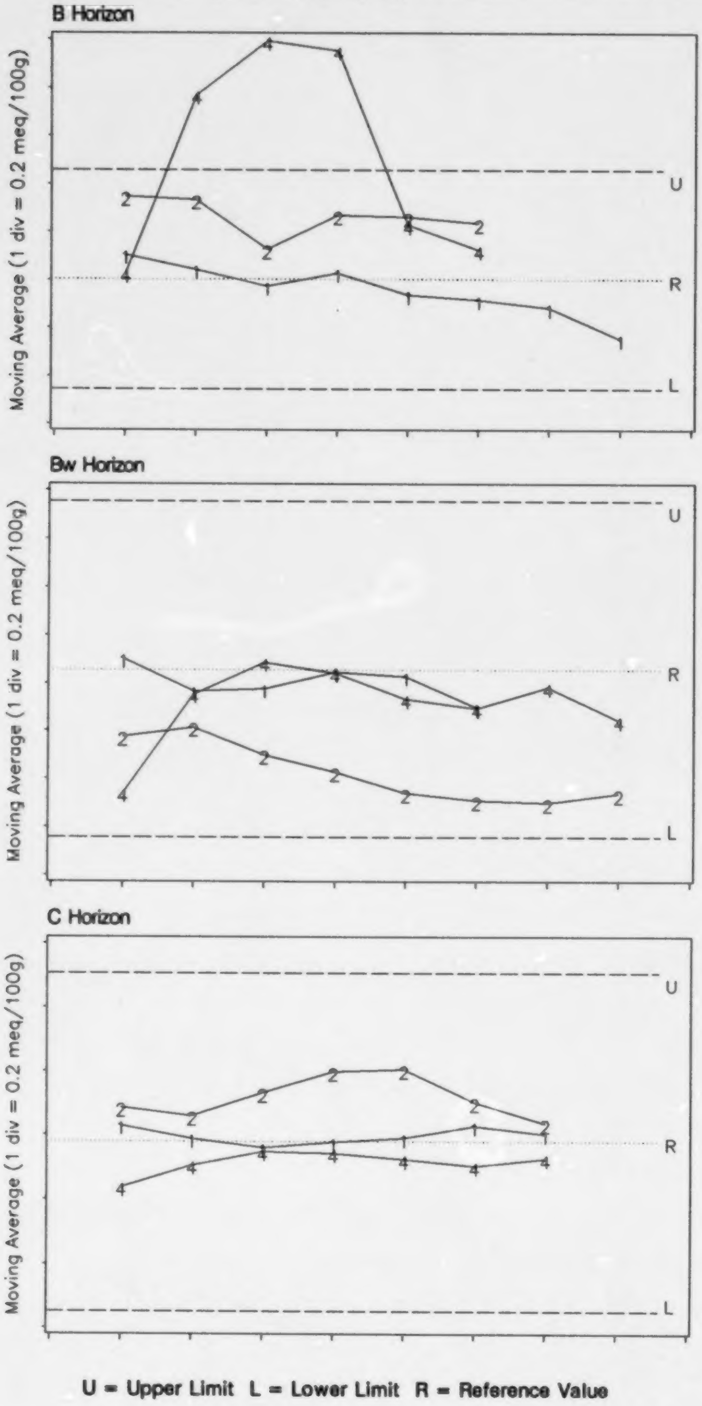


Figure I-24. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for CEC_CL.

CEC_OAC

Cation Exchange Capacity by Ammonium Acetate

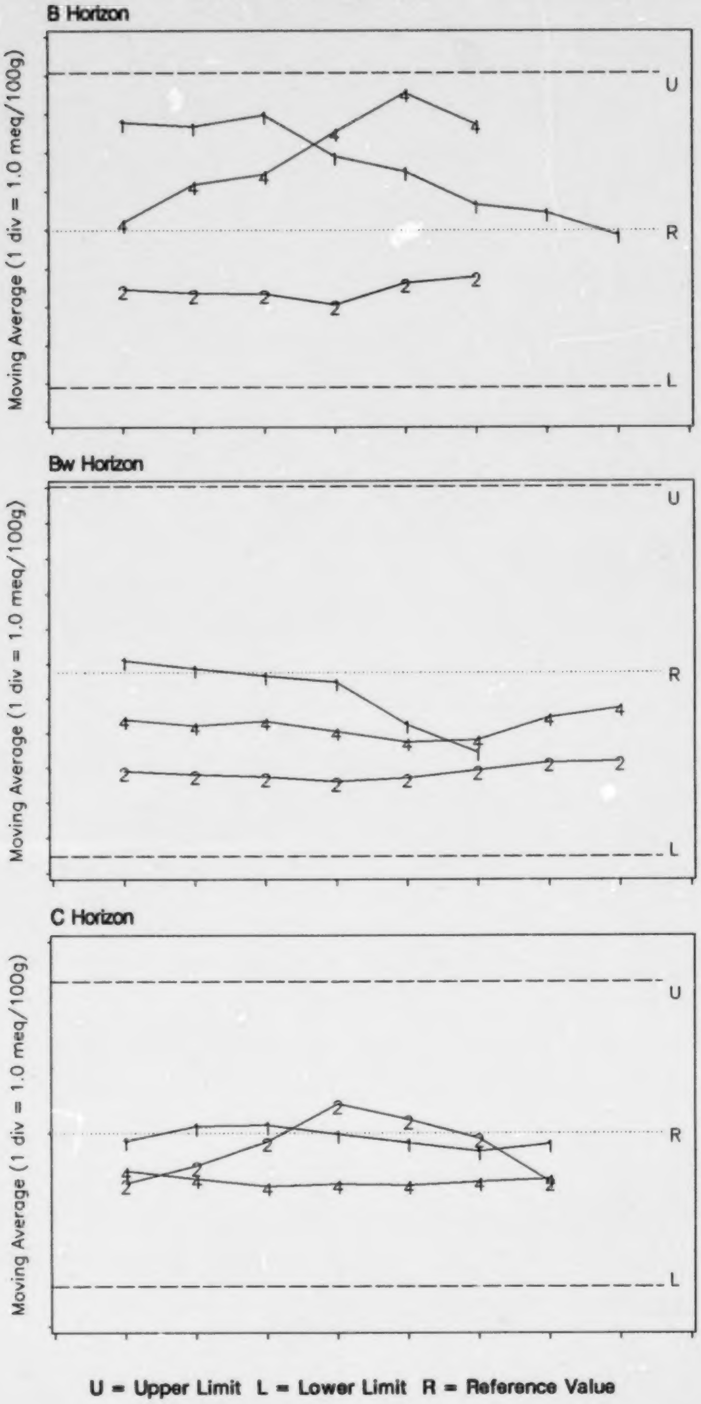
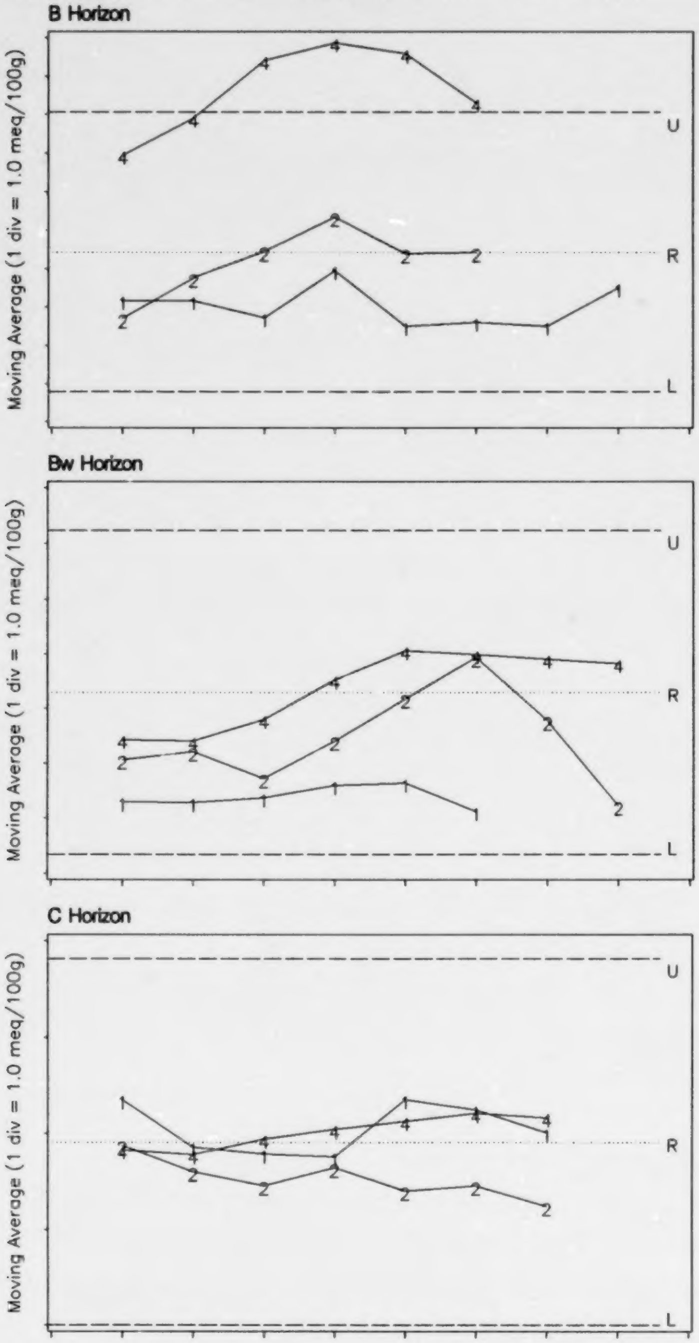


Figure I-25. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for CEC_OAC.

AC_BACL

Exchangeable Acidity in Barium Chloride Triethanolamine



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-26. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for AC_BACL.

CA_CL2

Extractable Calcium in Calcium Chloride

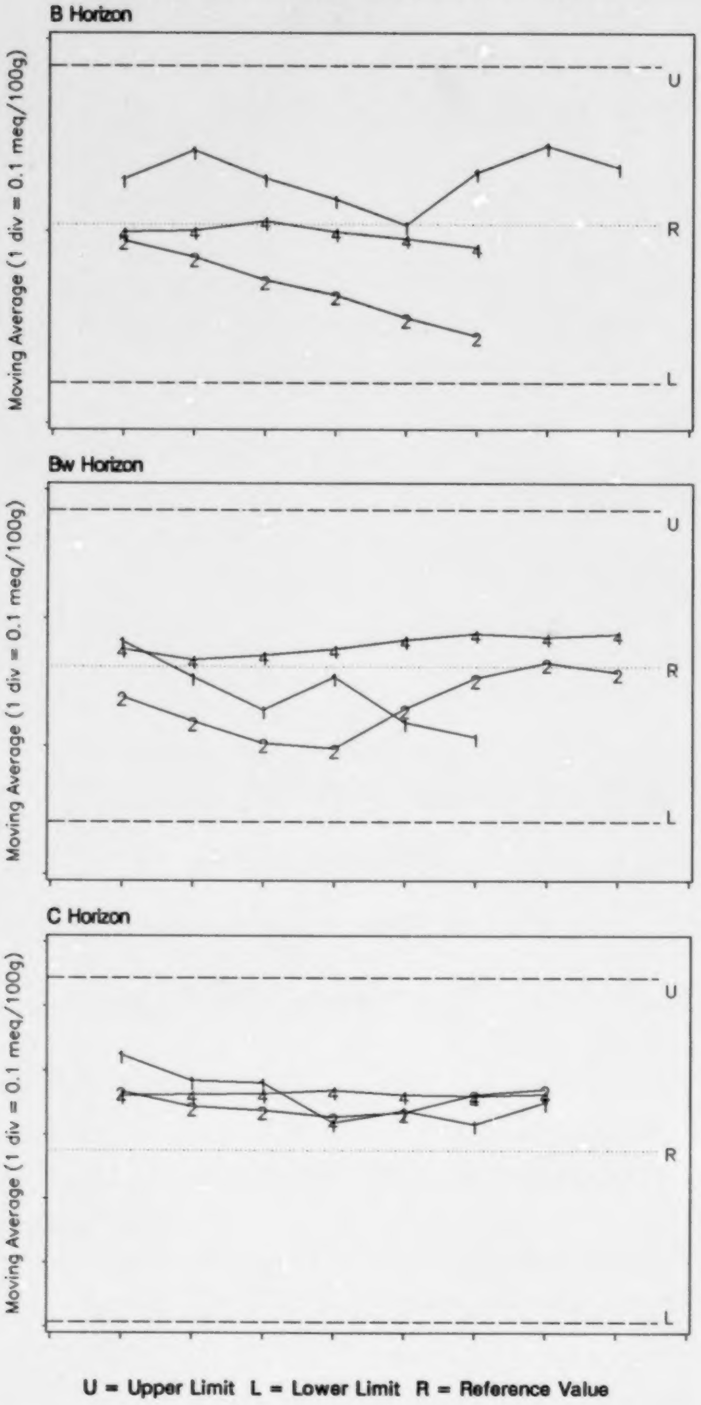


Figure I-27. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for CA_CL2.

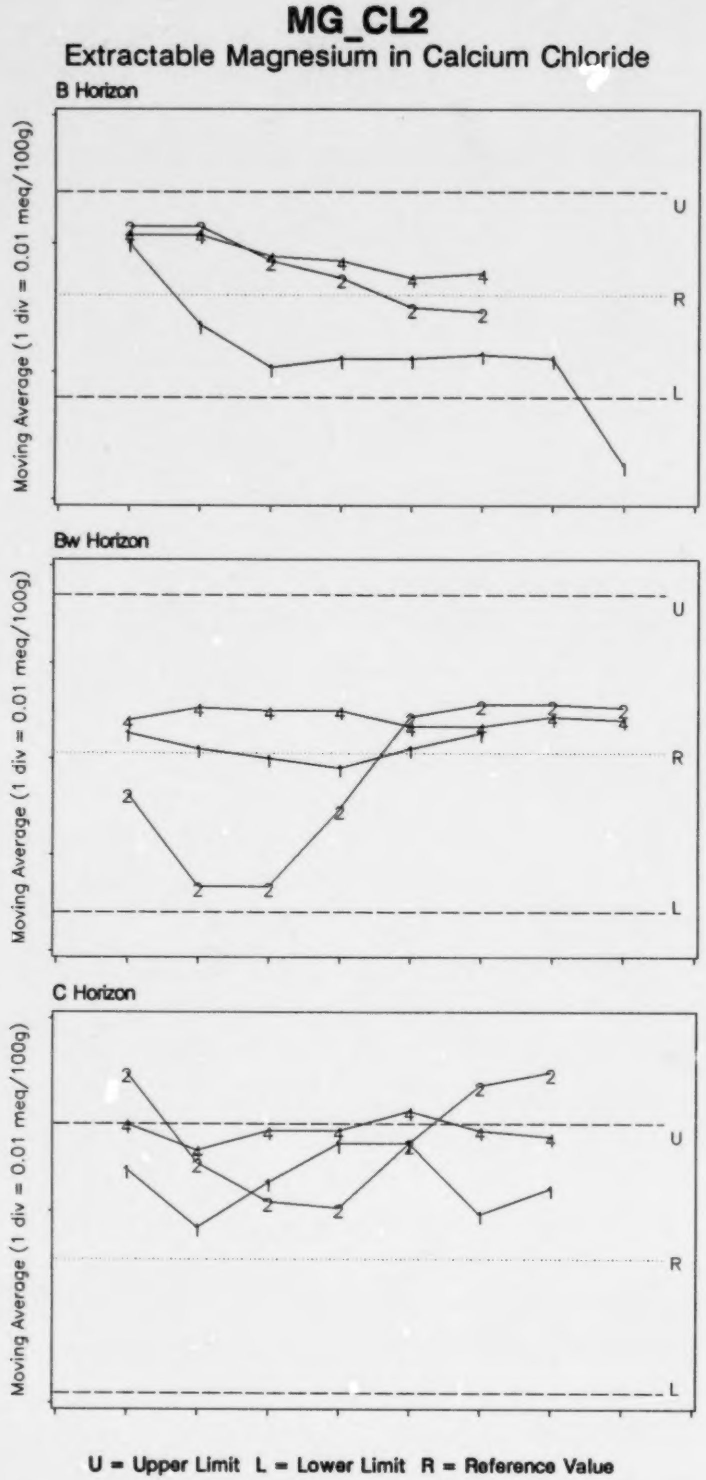
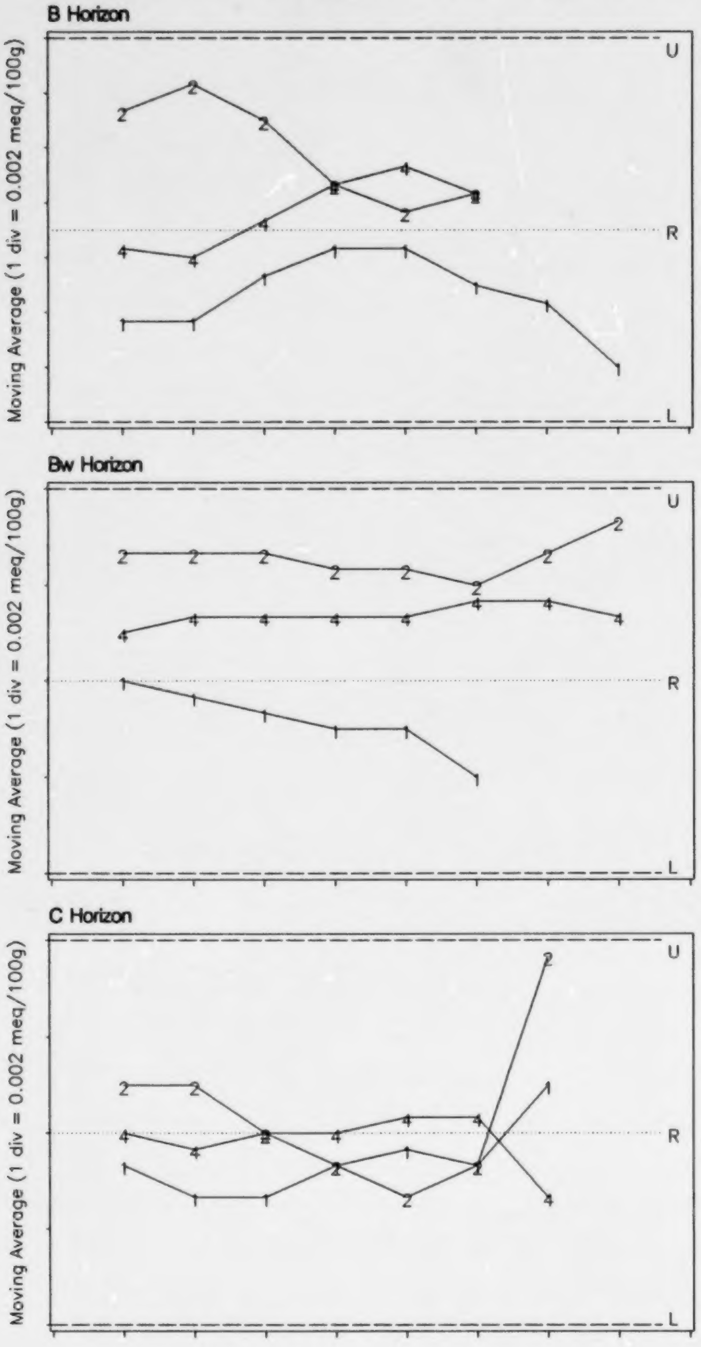


Figure I-28. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for MG_CL2.

K_CL2

Extractable Potassium in Calcium Chloride

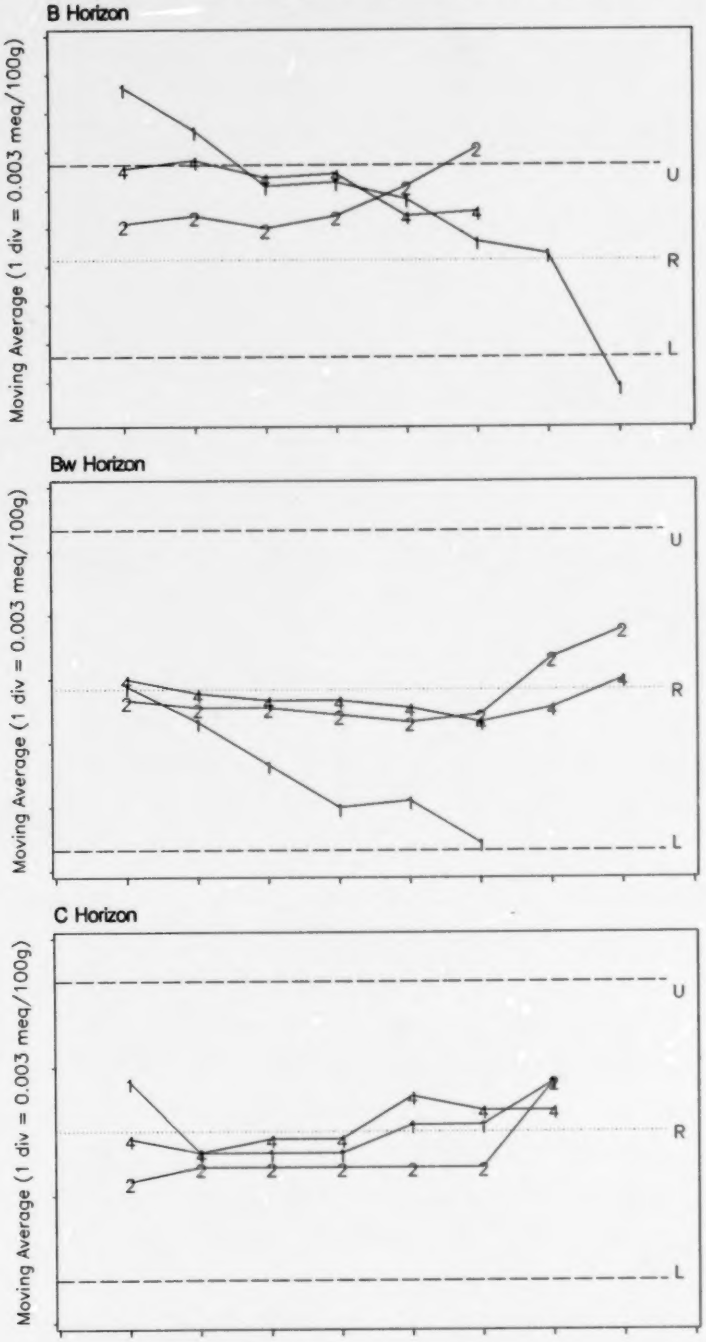


U = Upper Limit L = Lower Limit R = Reference Value

Figure I-29. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for K_CL2.

NA_CL2

Extractable Sodium in Calcium Chloride



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-30. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for NA_CL2.

FE_CL2
Extractable Iron in Calcium Chloride

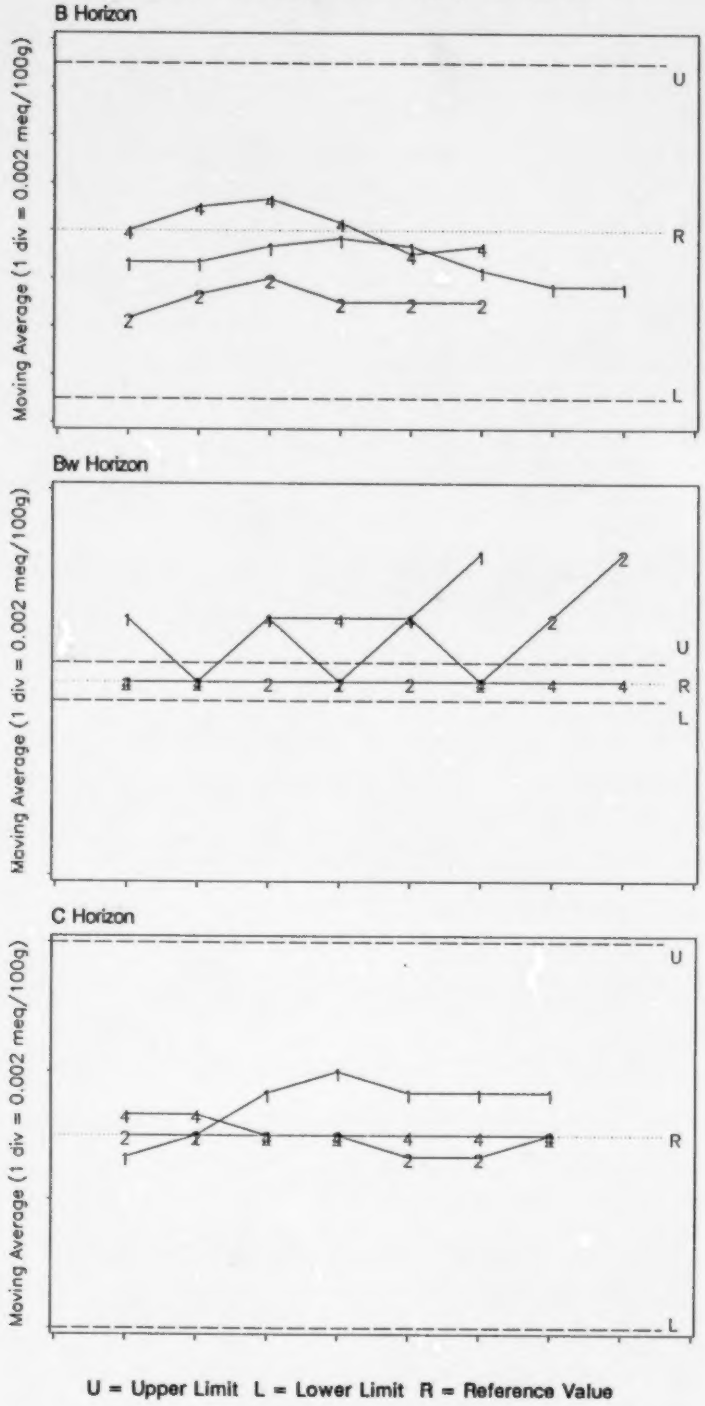
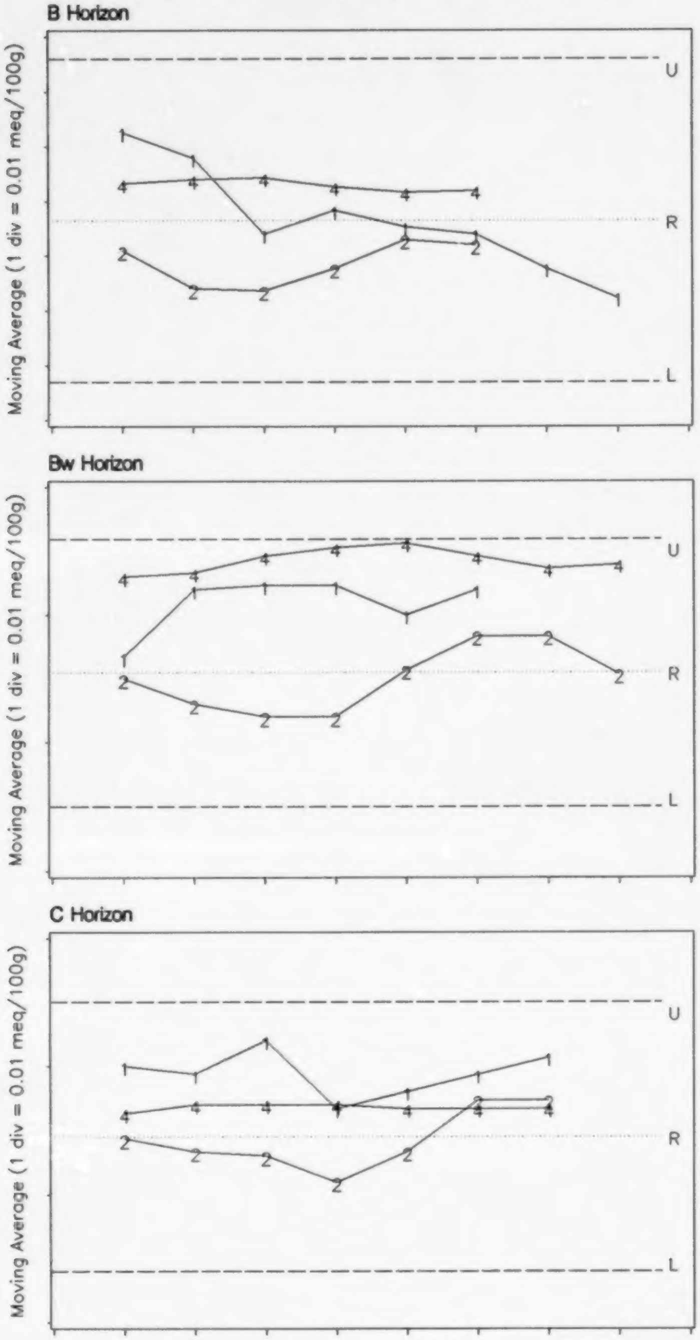


Figure I-31. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for FE_CL2.

AL_CL2

Extractable Aluminum in Calcium Chloride



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-32. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for AL_CL2.

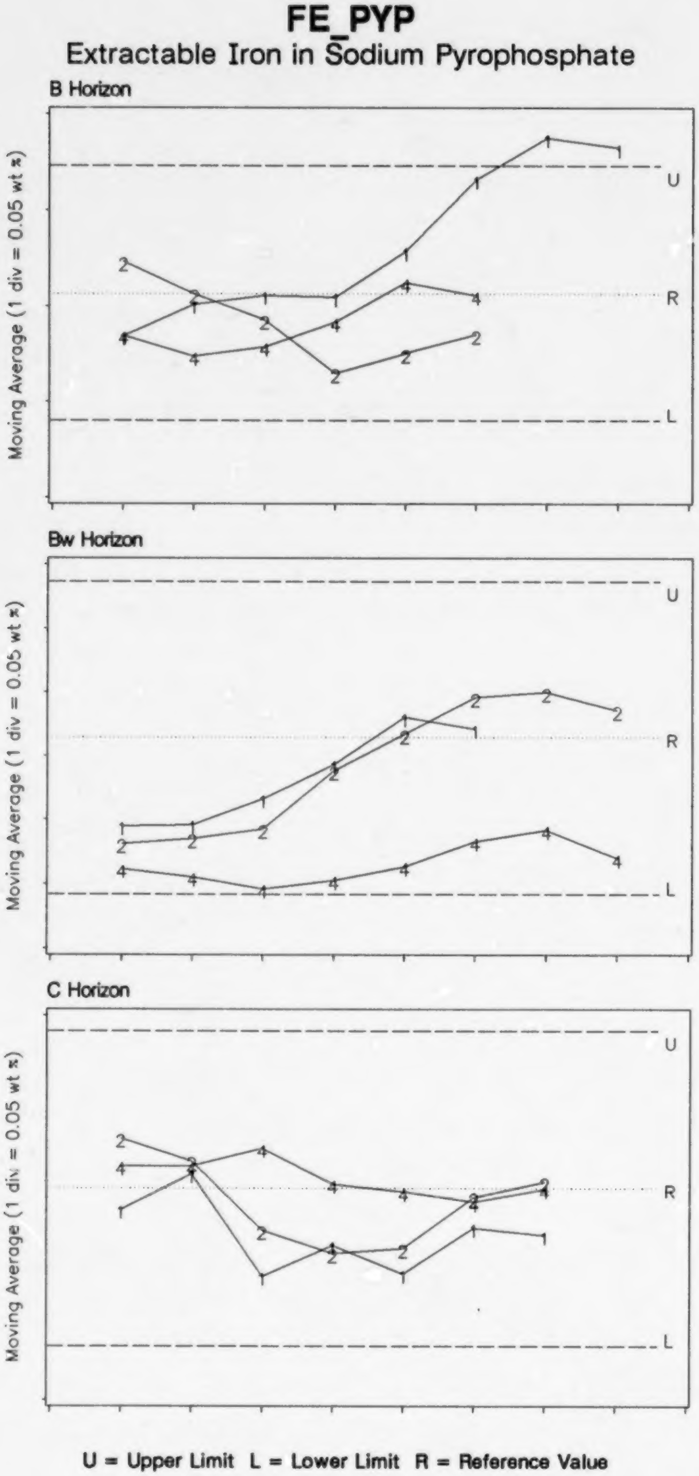
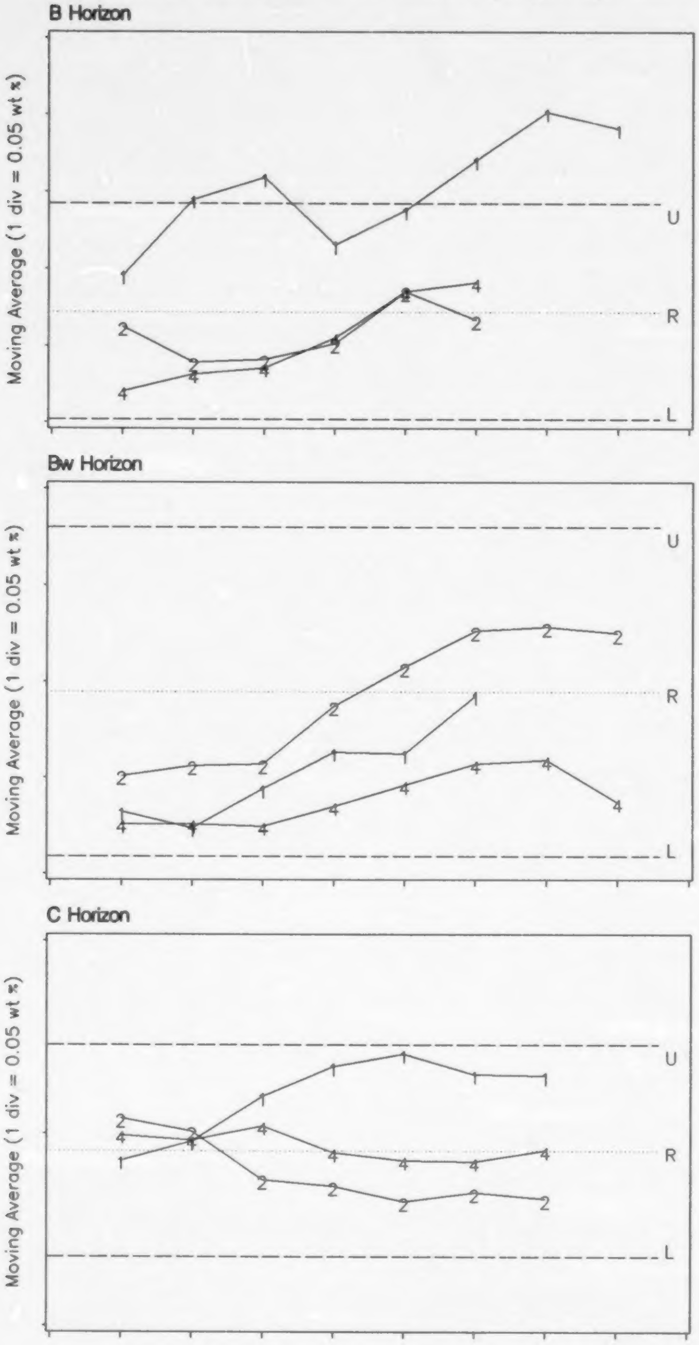


Figure I-33. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for FE_PYP.

AL_PYP

Extractable Aluminum in Sodium Pyrophosphate



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-34. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for AL_PYP.

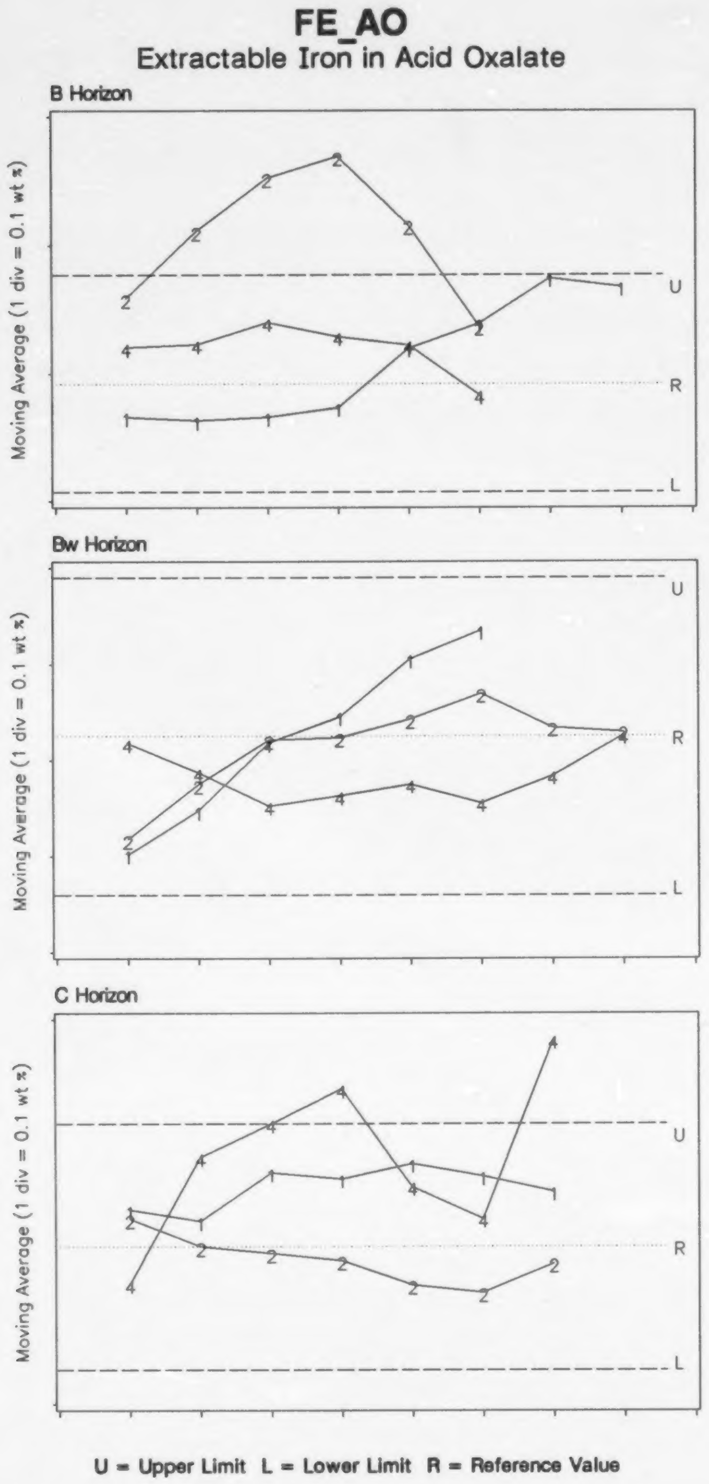
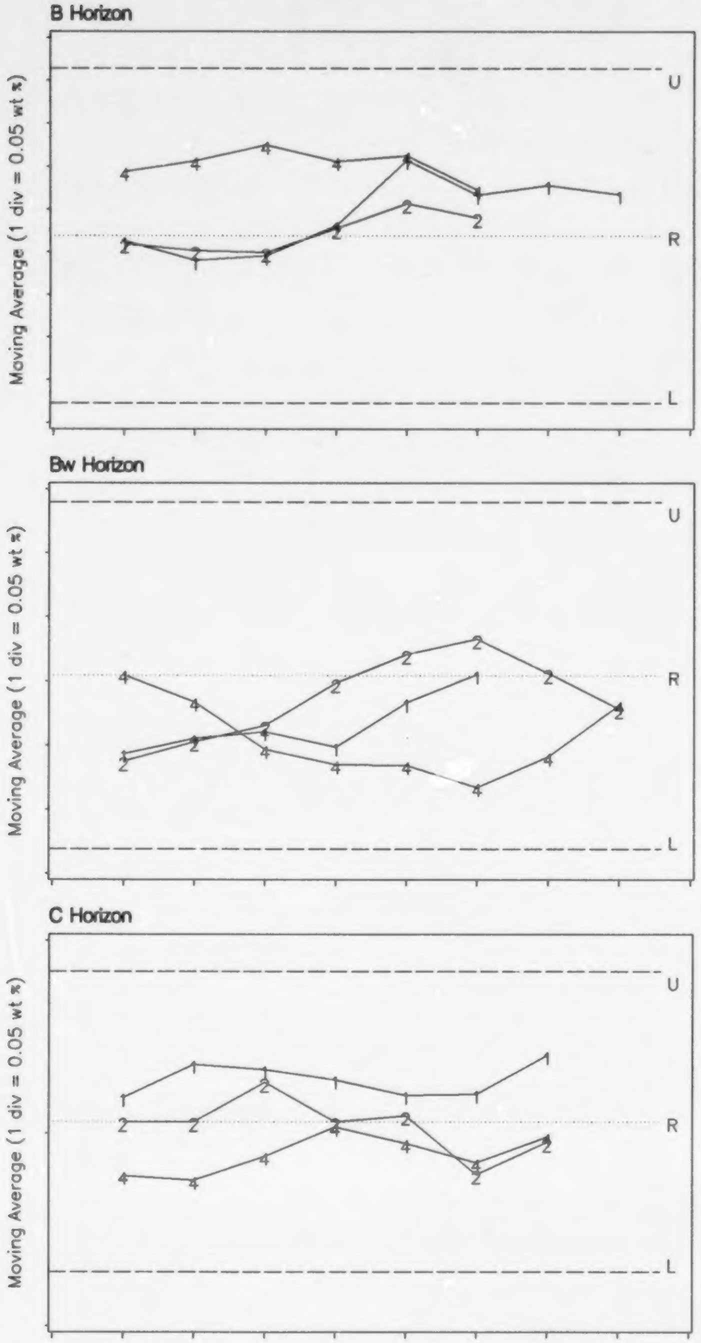


Figure I-35. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for FE_AO.

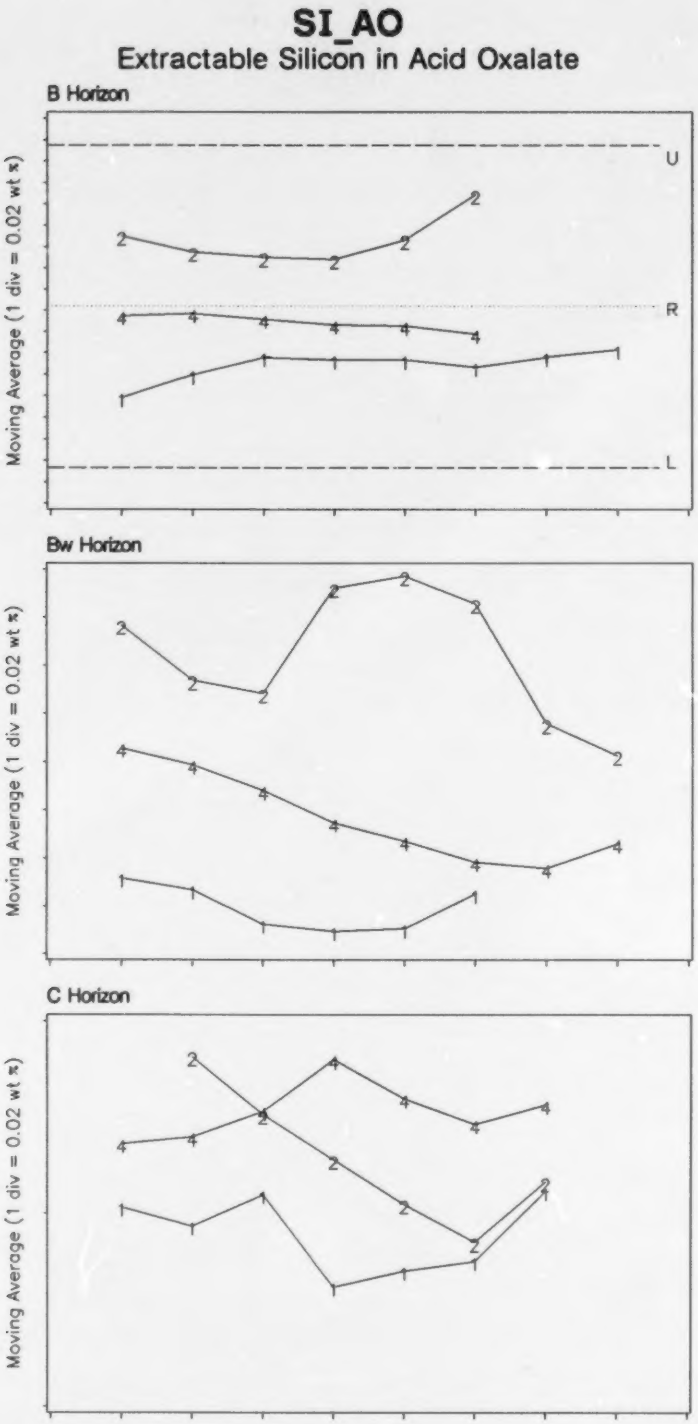
AL_AO

Extractable Aluminum in Acid Oxalate



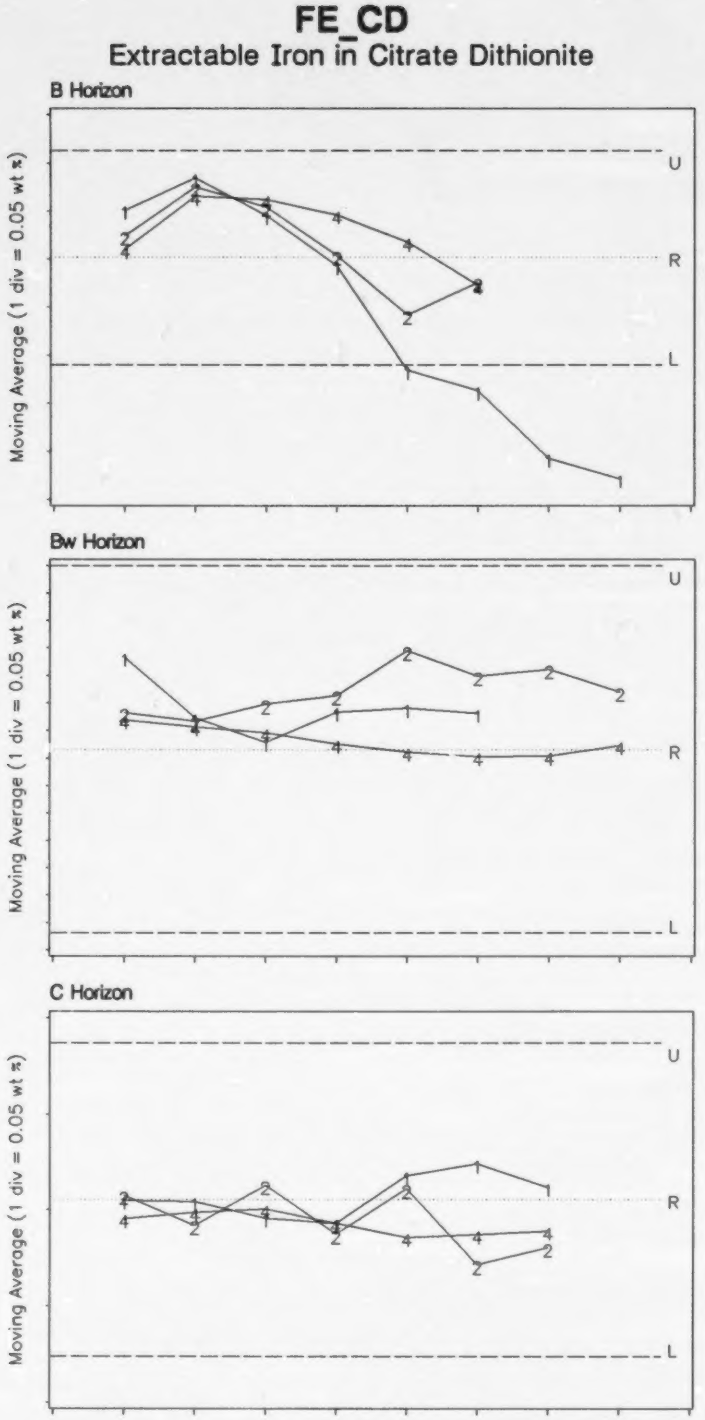
U = Upper Limit L = Lower Limit R = Reference Value

Figure I-36. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for AL_AO.



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-37. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SI_AO.



FE_CD

Extractable Iron in Citrate Dithionite

U = Upper Limit L = Lower Limit R = Reference Value

Figure I-38. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for FE_CD.

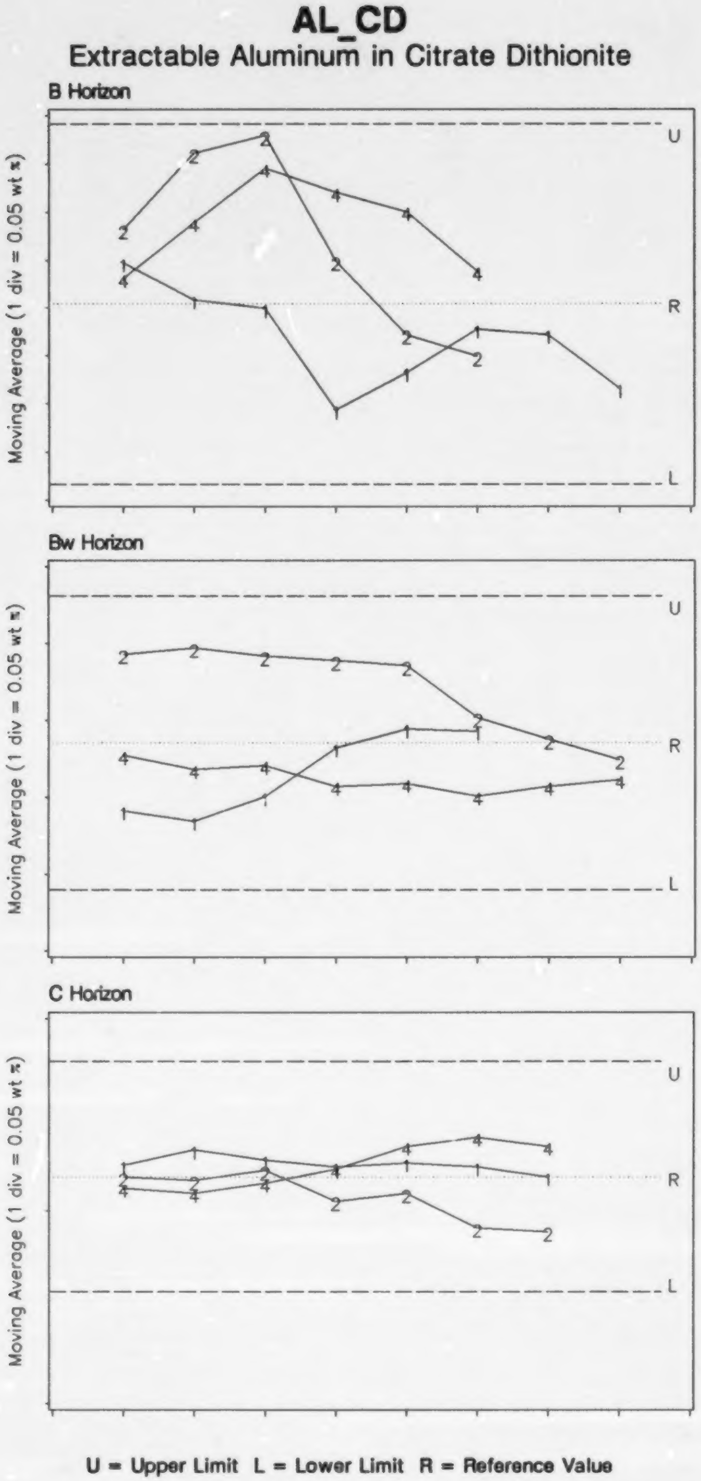
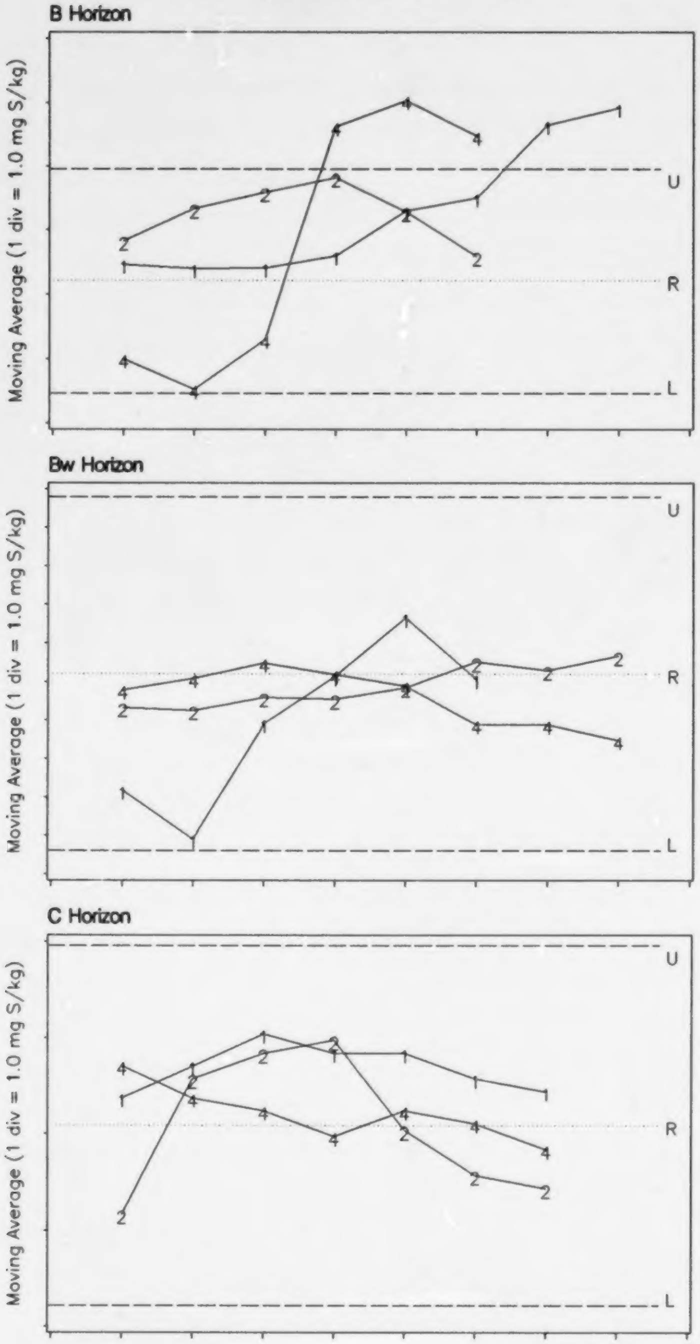


Figure I-39. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for AL_CD.

SO4_H2O

Extractable Sulfate in Water

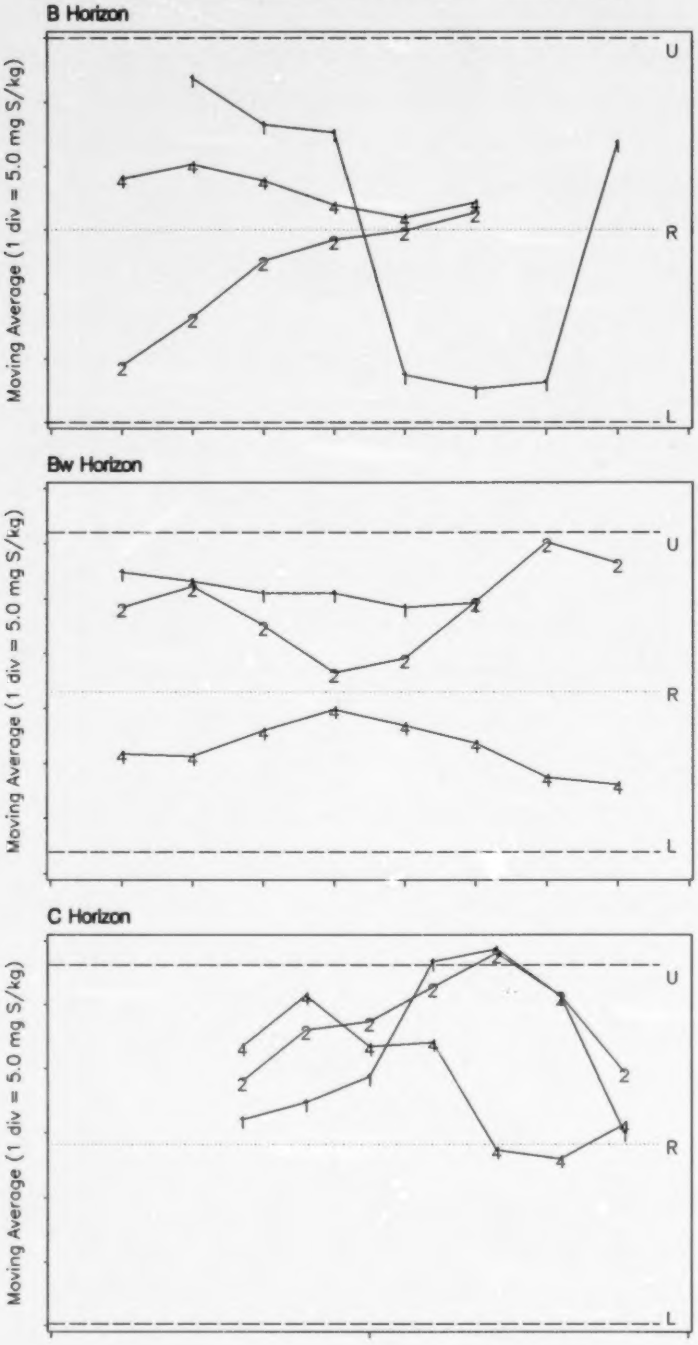


U = Upper Limit L = Lower Limit R = Reference Value

Figure I-40. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SO4_H2O.

SO4_PO4

Extractable Sulfate in Sodium Phosphate



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-41. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SO4_PO4.

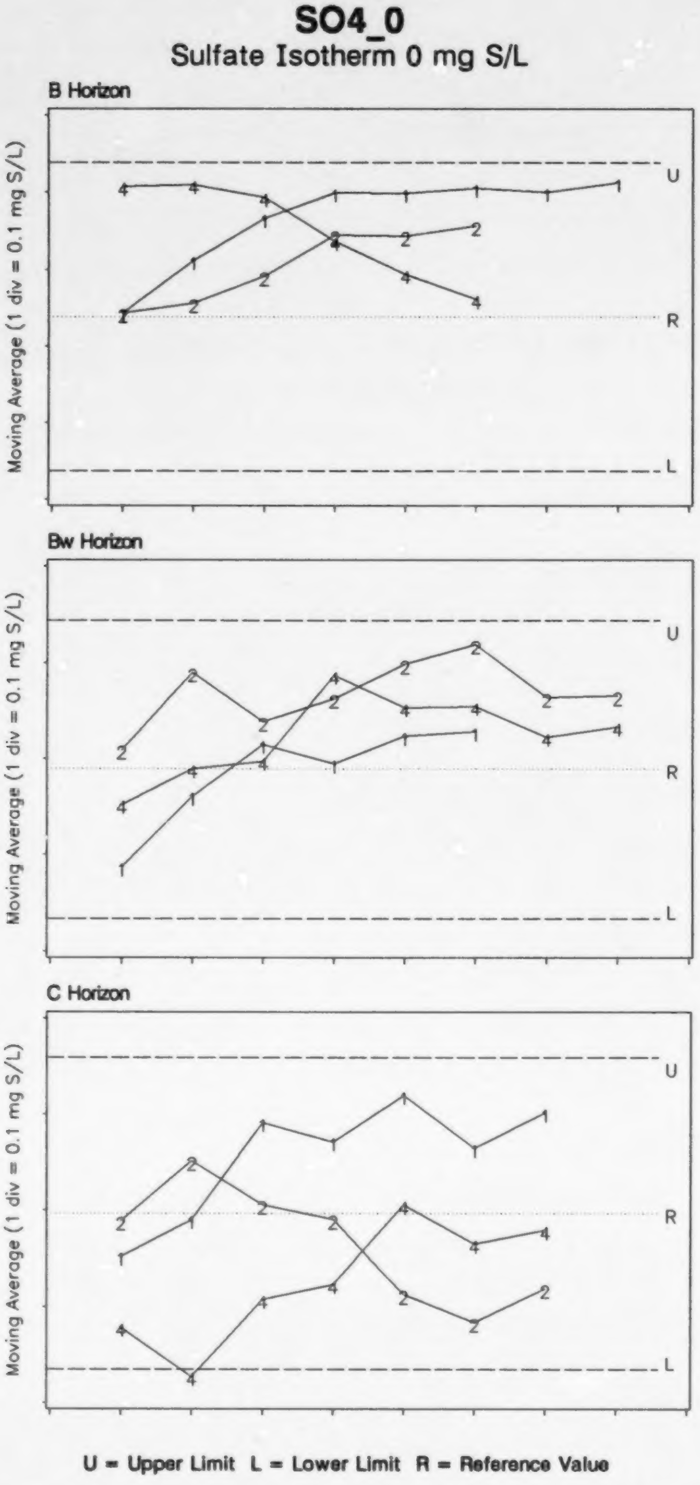
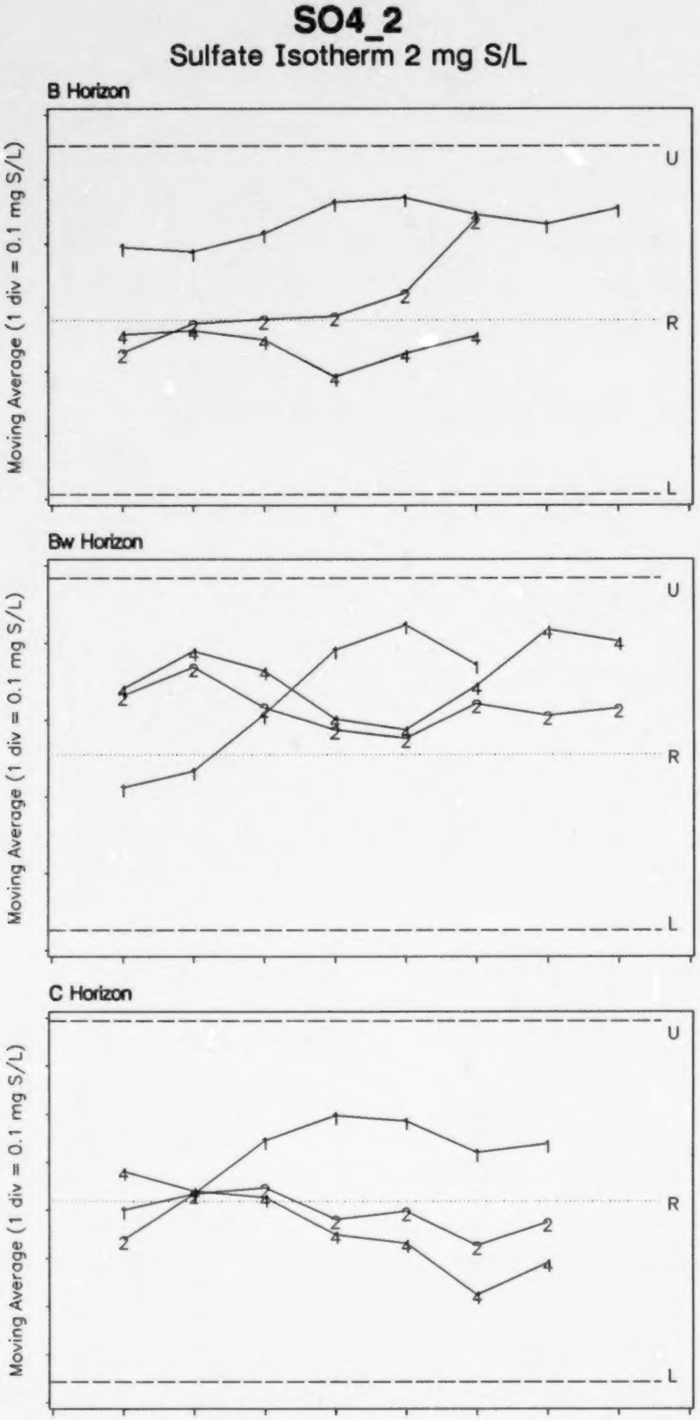


Figure I-42. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SO4_0.



SO4_2

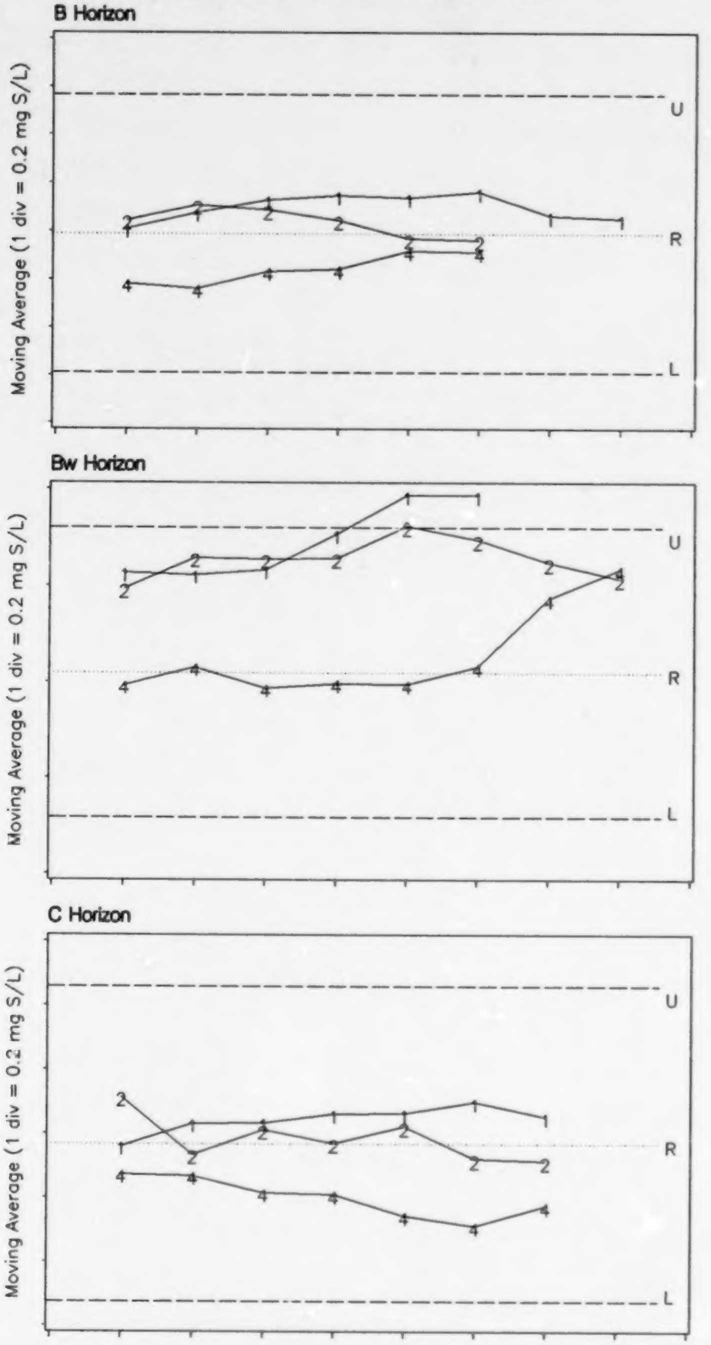
Sulfate Isotherm 2 mg S/L

U = Upper Limit L = Lower Limit R = Reference Value

Figure I-43. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SO4_2.

SO4_4

Sulfate Isotherm 4 mg S/L



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-44. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SO4_4.

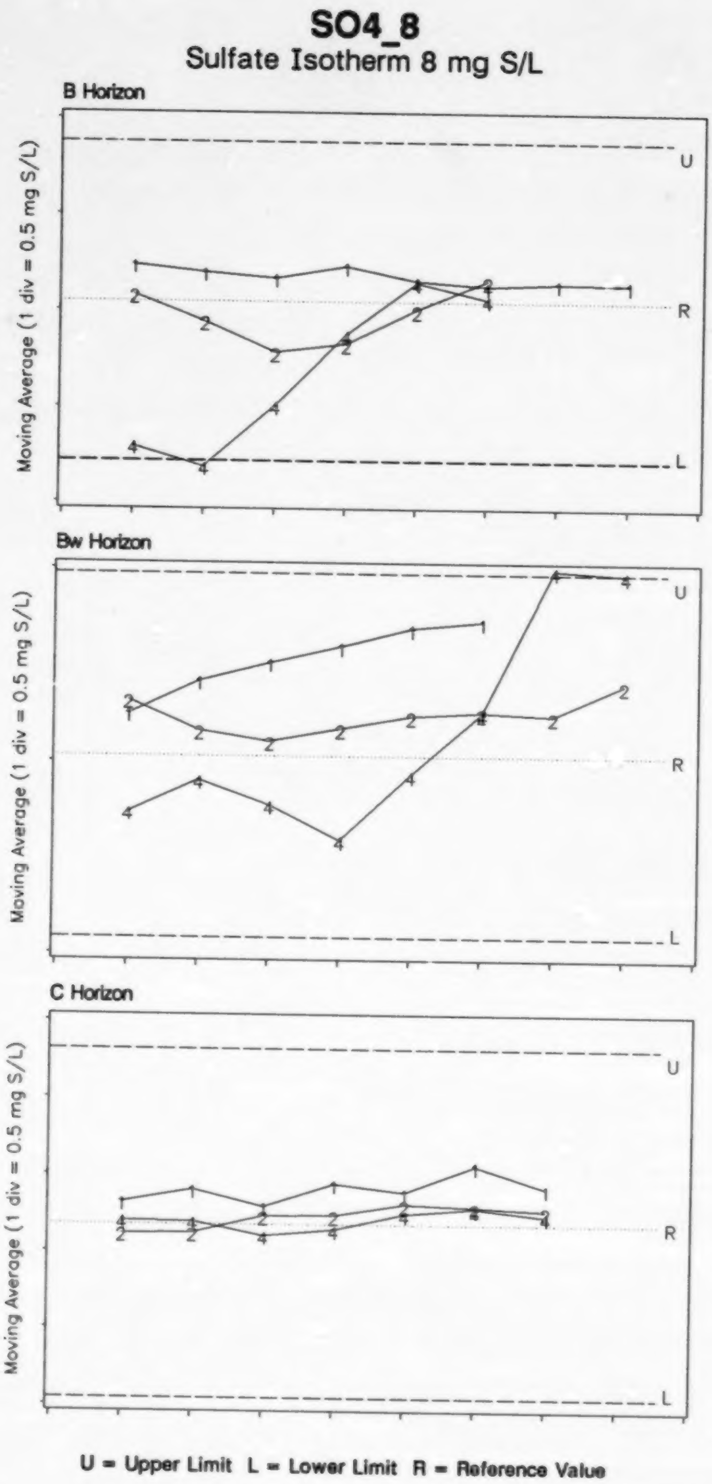


Figure I-45. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SO4_8.

SO4_16

Sulfate Isotherm 16 mg S/L

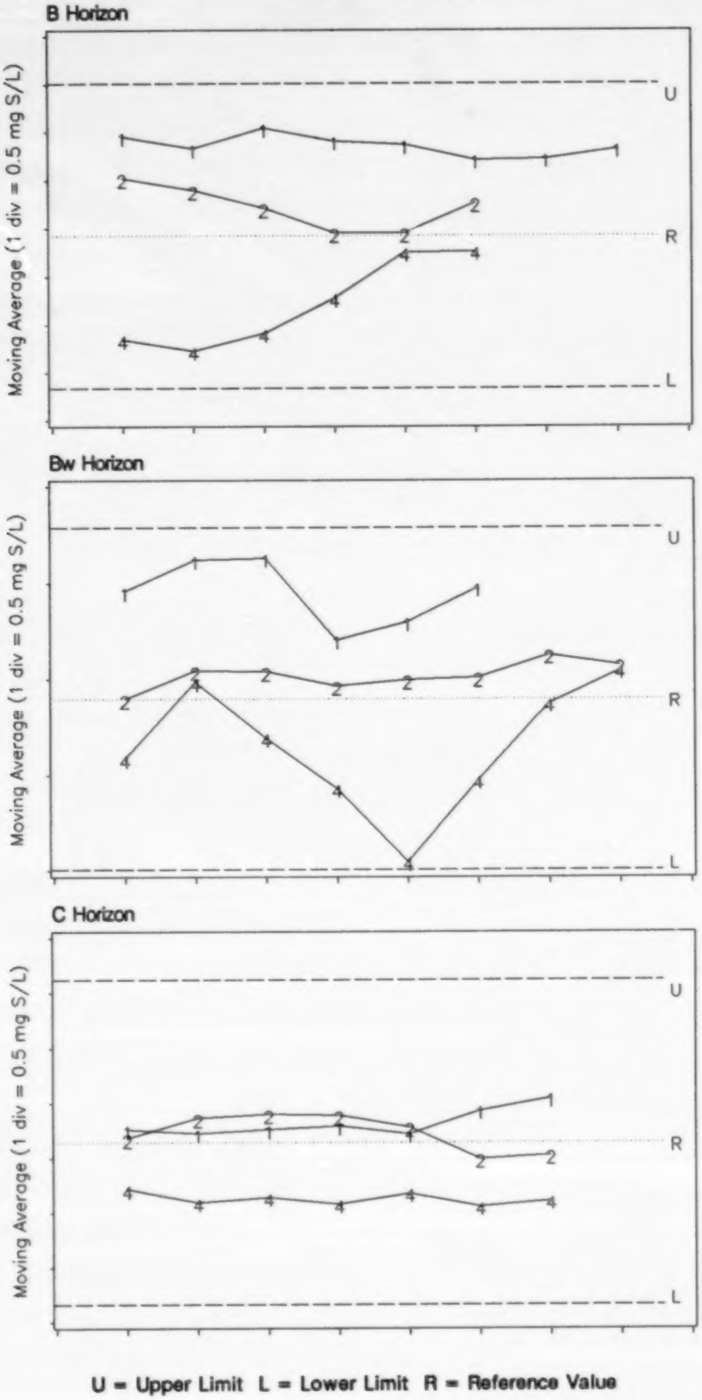
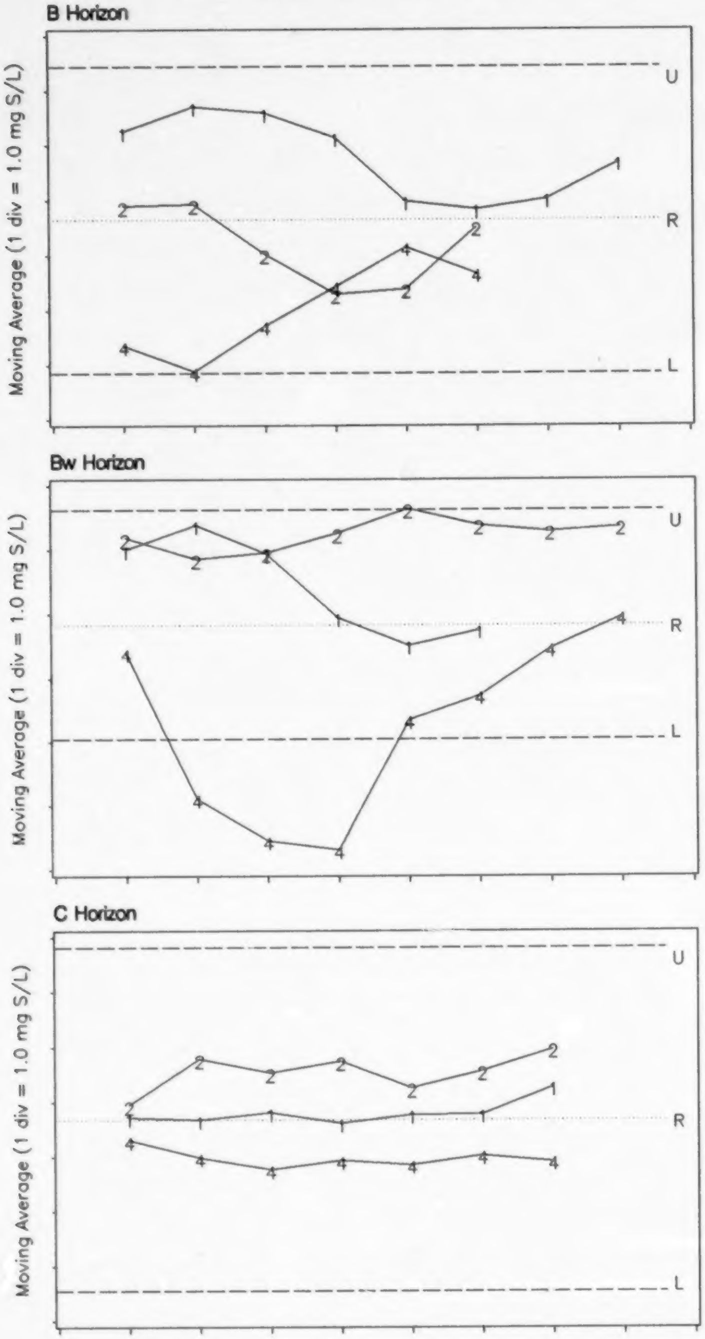


Figure I-46. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SO4_16.

SO4_32

Sulfate Isotherm 32 mg S/L



U = Upper Limit L = Lower Limit R = Reference Value

Figure I-47. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for SO4_32.

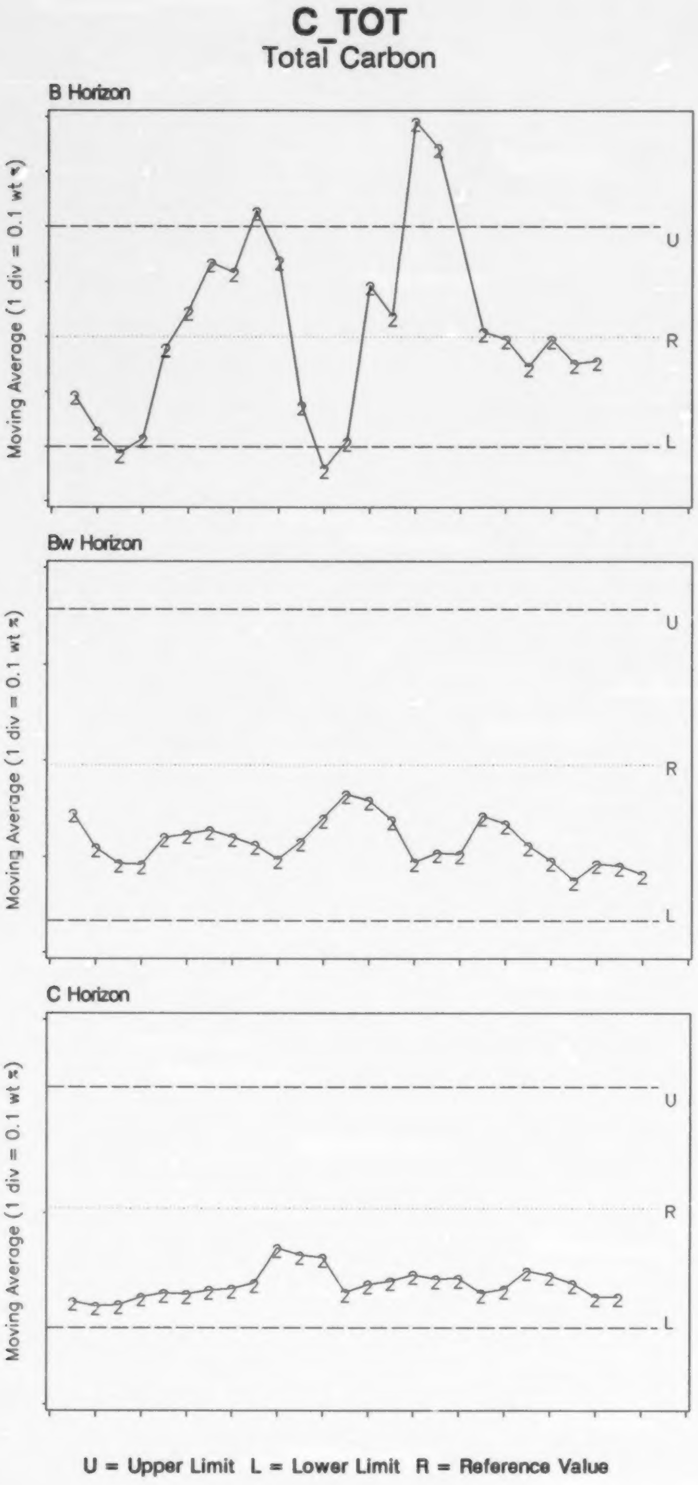


Figure I-48. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for C_TOT.

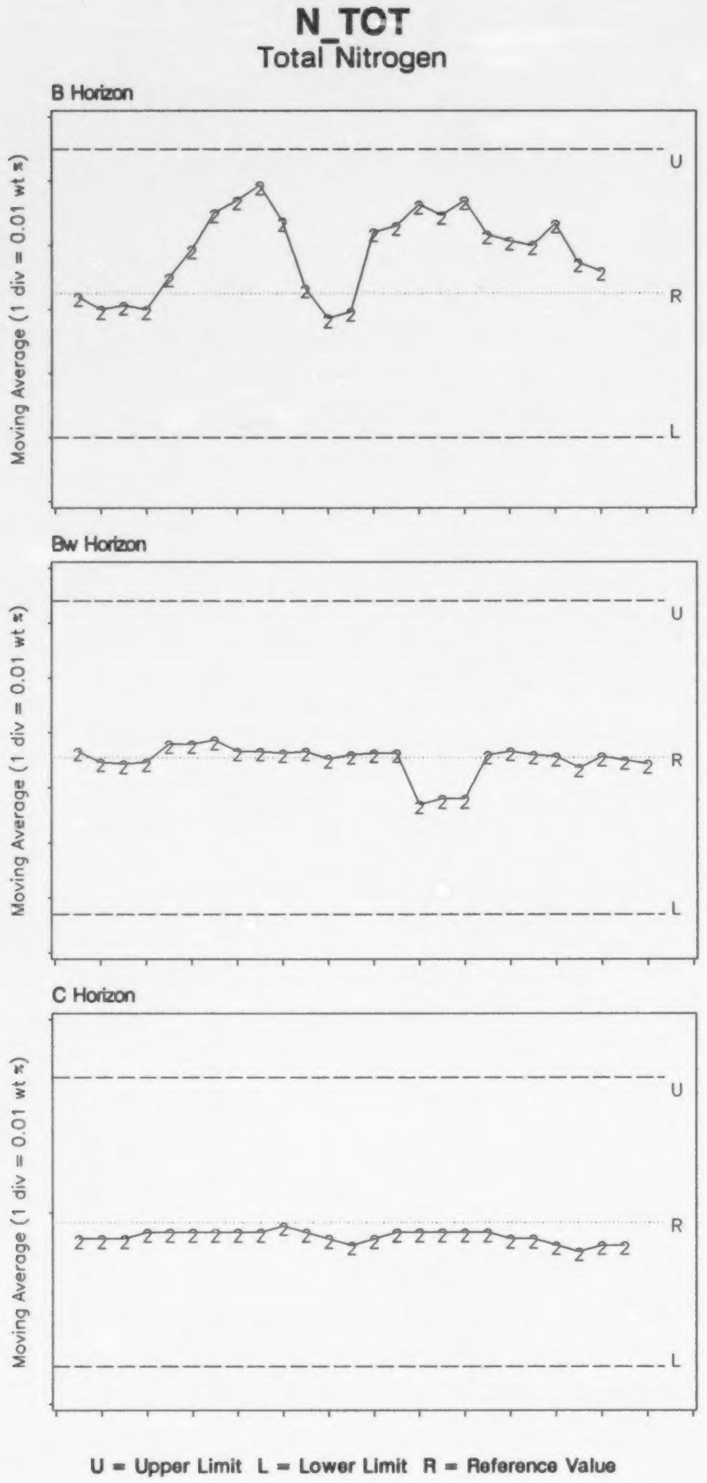


Figure I-49. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for N_TOT.

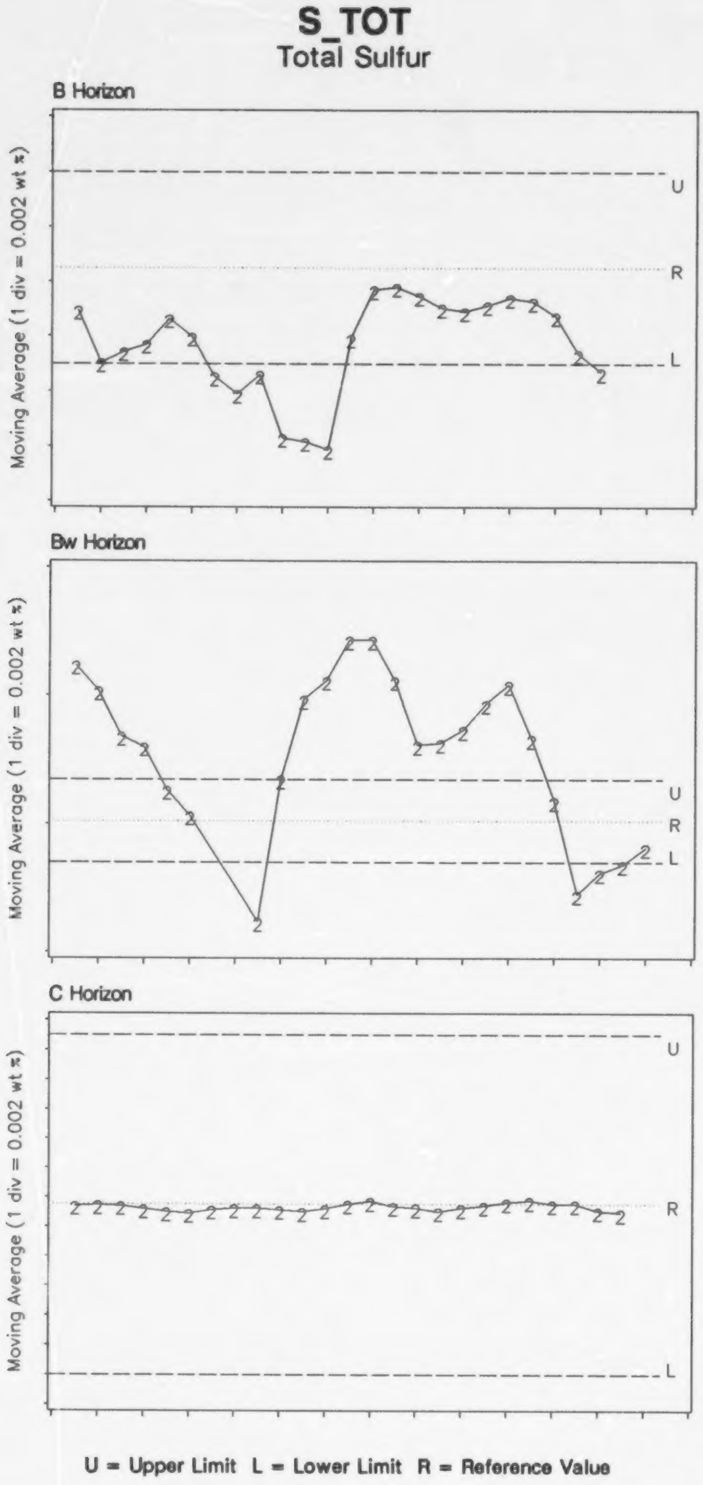


Figure I-50. Moving average plots of laboratory trends in B, Bw, and C horizon audit samples for S_TOT.

Appendix J

Step Function Approach for Estimating Data Uncertainties

The following internal report describes the step function approach that was used by the quality assurance staff for estimating the uncertainty from data collection error. A linear model is used to define measurement imprecision and bias as the principal quantitative characteristics of measurement uncertainty quantified during the routine data analysis. In addition, estimates are made of confounded population and measurement uncertainty as a function of specific configurations of regional soils data. Induced uncertainties at different data collection stages are estimated using soil chemistry data from replicate samples and audit samples.

Internal Report

Step Function Approach for Estimating Data Uncertainties

M. J. Miah, R. D. Van Remortel, G. E. Byers, M. L. Papp, and J. E. Teberg, Lockheed Engineering & Sciences Company, Las Vegas, Nevada, and L. J. Blume, U.S. Environmental Protection Agency, Las Vegas, Nevada.

Introduction

The effect of measurement error on the overall quality of environmental data should be carefully evaluated because of the potential for this error to influence the results of a study. The measurement error can be considered to be the sum of several components of error that occur at different, independent stages of the data collection process. The error can be characterized using data from a large number of replicate measurements within the sample population. Budgetary and logistical constraints, however, usually do not allow replication of each sample measurement. The next best alternative is to select a representative subsample of the routine samples for replication purposes.

Measurement error can be defined as a random variable or, in some cases, as a sequence of random variables. The error characteristics can be expressed as various combinations of the random variables. For this study, the primary characteristics that are associated with the measurement uncertainty are imprecision and inaccuracy [1]. Using an additive model, the observed characteristic of a routine sample is assumed to be the sum of the true sample characteristic and a random value of the measurement error. The imprecision is defined as the variance of the measurement error and the inaccuracy is defined as the bias, or expected value of the measurement error. The overall measurement uncertainty of a data set is a function of its measurement imprecision and inaccuracy.

In any quality assurance design, the data generation process should be controlled or managed in such a way as to achieve predetermined measurement quality objectives with respect to the error characteristics. For certain parameters, imprecision and inaccuracy may vary across the range of observed analyte concentration. In this event, it is possible to segment the entire concentration range into a series of different, mutually exclusive intervals. Imprecision and inaccuracy can be estimated for each interval of observed analyte concentration and all of the individual estimates can be combined to provide a pooled estimate of overall measurement uncertainty.

Operational Framework

The quality assurance design described herein was developed for use in a soil characterization study of various watersheds in the Mid-Appalachian region of the United States. The study is the third in a series of three regional surveys conducted as part of the U.S. Environmental Protection Agency's "Direct/Delayed Response Project". The objective of the project is to make regional predictions of the response time of various lake and stream watersheds to current or projected rates of acidic deposition. The two previous studies focused on the Northeastern region and Southern Blue Ridge region of the United States.

In the Mid-Appalachian survey, soil sampling classes were configured on the basis of intensive soil mapping conducted in the region. Each sampling class consists of discrete soil types, having similar geomorphic and developmental characteristics, which are grouped together to provide a representative sampling base across watersheds within the region. Soil pits are excavated at randomly selected sites within the appropriate sampling classes, and soil samples are collected from the component soil horizons within each exposed pedon. It is expected that the soil physical and chemical characteristics of samples from different pedons belonging to a specific sampling class are influenced by the horizon type and by natural spatial variability. It is also possible that overall measurement uncertainty is dependent on a specific soil characteristic.

The quality assurance design must be versatile enough so that the measurement uncertainty can be estimated irrespective of its dependence upon soil characteristics or configurations of soil variables. For this study, a modified hierarchical design [2] is used to estimate overall measurement uncertainty for the soil characteristics of interest. This approach assumes that the errors associated with different measurement operations are independent of each other. Measurement errors in the survey are generated during three independent operations: field sampling, sample preparation, and sample analysis. The generalized model used in the quality assurance design is as follows:

$$Y = X + \epsilon$$

where: Y is the observed value of a soil characteristic in a soil sample,
X is the true value of the characteristic in that sample, and
ϵ is the measurement uncertainty confounded in the sample,

and the primary components of the measurement uncertainty, ϵ, are defined as:

$$\epsilon = \epsilon_f + \epsilon_p + \epsilon_a$$

where: ϵ_f is the field sampling error,
ϵ_p is the sample preparation error, and
ϵ_a is the sample analysis error.

Assessment of Precision

The imprecision components of the measurement error are estimated through an analysis of variance (ANOVA), where the variance of the measurement error, $V(\epsilon)$, is defined in the following relationship:

$$V(\epsilon) = \sigma^2_f + \sigma^2_p + \sigma^2_a$$

where: σ^2_f is the variance from field sampling error,
σ^2_p is the variance from sample preparation error, and
σ^2_a is the variance from sample analysis error.

A three-stage sample design was implemented in the Mid-Appalachian survey. Using this approach, a soil horizon from every third pedon sampled in the survey was selected for replication. Each of these horizons was sampled in duplicate to produce a field duplicate/routine pair of samples (first stage). Each of the two samples was subsequently homogenized and subdivided into preparation/field duplicate and preparation duplicate/routine subsamples, respectively, at a preparation laboratory (second stage). The resulting four samples that correspond to the originally selected horizon were randomly placed in one group, or batch, of analytical samples. The batch was analyzed completely by one analytical laboratory (third stage). In all, 29 batches were analyzed during the survey. All of the soil samples were processed by one preparation laboratory and analyzed among three analytical laboratories. Approximately equal numbers of replicate samples were randomly allocated to each analytical laboratory; therefore, imprecision estimates should be equally reliable among the laboratories.

Normally, a complete hierarchical design would require another level of replication at this third stage of measurement; however, past experience has shown that laboratory analysts can easily identify the origin of these soil replicates, called analytical duplicates, and might make a conscious effort to reduce the analytical variability for the replicate measurements. As a result, the third-stage analytical duplicates are not utilized in this portion of the modified hierarchical design; instead, double-blind [3] laboratory audit samples are used as surrogates to estimate the sample analysis imprecision. Nonetheless, replication data under the modified design are sufficient to estimate overall measurement imprecision, field sampling imprecision, and confounded sample preparation/analysis imprecision.

For this study, suppose that measurement imprecision changes with the value of a soil characteristic. The true value (X) of the characteristic, as defined in the general model above, can be considered a random variable upon which the measurement imprecision may be dependent. The error variance, $V(\epsilon)$, in this case would be appropriate only for a given analyte concentration, X_0. Hence, the variance is a function of analyte concentration and the quantity $\sigma^2 (\epsilon | X = X_0)$ can be defined as the conditional error variance at the given analyte concentration. The imprecision related to each member of the data set $\{X_i\}_{i=1,n}$, which spans the entire range of analyte concentrations for the routine samples, can be estimated. These individual estimates can be pooled in order to derive a single estimate of overall measurement imprecision that becomes conditional if data within one or more levels of concentration are missing.

The ANOVA for replicate sample data provides an estimate of overall measurement imprecision as well as an estimate of the specific imprecision associated with the field sampling and laboratory operations. At this juncture, the sample preparation and sample analysis imprecision are confounded and cannot be separated. An ANOVA table identifying the variance components is provided in Table 1 below.

Table 1. Analysis of Variance Components

Sources of variance	Sum of square	df	Mean square	Expected value of the mean square
Average	$nY_{\_}^2$	1		
Field duplicates	$\Sigma(Y_{ij} - Y_{i.})^2$	1	m_f	$2\sigma^2_f + \sigma^2_p + \sigma^2_a$
Preparation duplicates	$2\Sigma(Y_{i.} - Y_{\_})^2$	2	m_l	$\sigma^2_p + \sigma^2_a$
Total	Y_{ij}^2	4		

After obtaining an estimate of measurement imprecision for each duplicate/routine sample pair, it is necessary to combine the individual estimates to obtain a pooled estimate of measurement imprecision for the data set. A fundamental problem is that this estimate is dependent on the analyte concentration of the associated routine samples, i.e., the error variance becomes σ^2_i for the "i"th analyte concentration. A scatter diagram of the mean of replicate measurements versus the error variance can provide a useful approximation of the relationship between analyte concentration and measurement imprecision. It may be that the relationship is not very distinct except for an indication that measurement imprecision varies with changes in the observed analyte concentration, such that:

$$\sigma^2 : \Omega \rightarrow (0,K]$$

where: Ω is the set on which the routine sample observations take values, and
K is the highest variance in the range.

The dominated convergence theorem is used to define a sequence of step functions $\phi_n = \Sigma_{[i=1,n]} \sigma^2_i \chi_{Fi}$, such that ϕ_n converges to σ^2 irrespective of its functional form [4]. The overall measurement imprecision is also a random variable belonging to the weighted partition $\{ F_i : \sigma^2_i \}_{i=1,n}$ for a large number of partitions. To regulate the effects of concentration dependency, the entire concentration range can be partitioned into n mutually exclusive intervals $F_1, F_2, \ldots F_n$. These intervals are not necessarily of equal concentration length and are such that within each interval, F_i, the error variance is independent of analyte concentration; therefore,

$$\cup F_i = \Omega, \text{ and } F_i \cap F_j = \Phi \text{ for all } i \neq j$$

where: Φ is an empty set.

From this, the expected variance can be defined in the following manner:

$$\begin{aligned} E(\sigma^2) &= \int \sigma^2\, dG \\ &= \Sigma_{[i=1,n]} \sigma^2_i\, E(\chi_{Fi}) \end{aligned}$$

where: χ_{Fi} is 1 (if $Y \in F_i$) or 0 (if $Y \in F_i^c$), and
G is a distribution function.

So, $E(\chi_{Fi}) = P(F_i)$
where: $P(F_i)$ is the proportion of routine samples within the interval F_i.

For every interval, the variance can be estimated from the replicate sample data set and the corresponding proportion can be estimated from the routine sample data set. Cluster analysis is useful for defining the number of intervals and their endpoints. The expected variance across intervals, as defined above, can be used as a measure of uncertainty due to imprecision. The rationale for this is as follows:

Scenario 1: Suppose it is found that imprecision is relatively constant for different analyte concentrations, i.e., there is no evidence for rejecting the hypothesis that $\sigma^2 = \Delta$, i.e., that $V(\epsilon)$ is a constant function on the routine data set Ω. Then:

$$\begin{aligned} E(\sigma^2) &= \int \sigma^2\, dG \\ &= \Delta\, \Sigma_{[i=1,n]}\ E(\chi_{Fi}) \\ &= \Delta\, \Sigma_{[i=1,n]}\ P(F_i) \\ &= \Delta, \text{ because } F_i \text{ and } F_j \text{ are disjoint for every } i \neq j, \\ &\qquad \text{and } P(\cup F_i) = P(\Omega) = 1 \end{aligned}$$

Scenario 2: Suppose it is found that imprecision is not constant for different analyte concentrations, i.e., there is no evidence for rejecting the hypothesis that $V(\epsilon)$ is a two-step function, as follows:

$$\sigma^2 = \begin{cases} \Delta_1 & \text{if } Y \in F_1 \\ \Delta_2 & \text{if } Y \in F_2 \end{cases}$$

$$\text{then: } \begin{aligned} E(\sigma^2) &= \int \sigma^2\, dG \\ &= \Sigma_{[i=1,2]} \Delta_i E(\chi_{Fi}) \end{aligned}$$

If $\alpha100$ percent of the routine samples is within F_1, the above expression becomes $E(\sigma^2) = \alpha\Delta_1 + (1\text{-}\alpha)\Delta_2$. The convex combination of Δ_1 and Δ_2 is a reliable estimate of measurement imprecision over the concentration range. In this scenario, $\alpha100$ percent of the routine data have imprecision equal to Δ_1 and $(1\text{-}\alpha)100$ percent of the data have imprecision equal to Δ_2.

Scenario 3: Suppose it is found that imprecision is continuously changing on the space Ω where the observed routine sample characteristic Y takes values.

Since $\sigma^2 \geq 0$, there exists a sequence of step functions, ϕ_n , as defined previously, such that ϕ_n increases to σ^2 for every characteristic in Ω, then:

$$\begin{aligned} E(\sigma^2) &= \int \sigma^2 \, dG \\ &\simeq \Sigma_{[i=1,n]} \sigma_i^2 \, E(\chi_{Fi}) \\ &= \Sigma_{[i=1,n]} \sigma_i^2 \, P(F_i), \end{aligned}$$

so the measure of imprecision remains valid irrespective of the functional form of the error variance on Ω .

It should be noted that the logistical constraints of the sample analysis procedures induced possible group effects due to the configuration of samples into batches. To assess these effects, the analytical imprecision components of ϵ can be expressed as the two independent segments of within-batch and between-batch imprecision. Each sample within a batch was likely to go through similar treatments and could reflect a unique batch effect. Likewise, a between-batch effect was likely to be random and was independent of the within-batch effect. These effects are solely a characteristic of the sample analysis stage and were designed to enable the evaluation of laboratories under a controlled condition, where a batch is used as the common measure of control, e.g., for a given day of analysis or by a single analyst.

The rationale behind these assumptions is that the manner in which one batch of samples is treated has no bearing on the manner in which the other batches of samples are treated, i.e., all samples are handled according to a standard operating procedure. One-way ANOVA of the audit sample data revealed that, at a given analyte concentration, the between-batch imprecision was usually larger than the within-batch imprecision. The overall measurement variance was calculated as the sum of the within-batch variance, $V_W(\epsilon)$, and between-batch variance, $V_B(\epsilon)$. The within-batch variance was estimated from the variations between duplicate samples that were contained in each batch which were subsequently pooled across all batches. The between-batch variance was estimated by calculating the pooled variation from the mean of the duplicate sample means across the batches.

Assessment of Accuracy

Besides imprecision, inaccuracy is the other primary aspect of data uncertainty. An effective quality assurance program should contain a built-in mechanism to control inaccuracy below a defined level. The design should also allow point and interval estimation of bias, identification of interlaboratory differences, and assessment of intralaboratory trends. For this study, bias is considered to be the quantitative element of inaccuracy used in estimating measurement uncertainty. Laboratory differences and trends are evaluated and used to describe the characteristics of accuracy in the data sets.

Estimation of Bias

Controlling bias in the data set is a fundamental problem of quality assurance. If bias is used as the primary quantitative measure of inaccuracy, then the presence of inaccurate data may indicate that there is nontrivial bias in the data set. In the Mid-Appalachian survey, contractual requirements for field and laboratory reference samples are used to control bias to a negligible level. To accomplish this, the mean sum of squares of the reference sample results should be small enough so that the measurement bias can be considered negligible with 95 percent confidence, that is:

$$|Y - X| \leq Z_{95} \sqrt{E(\sigma^2)}\ .$$

If the expected variance is known or can be estimated *a priori* by using reference data, then exception windows for the reference samples can be generated.

In the additive model, the bias component of measurement uncertainty is estimated through an analysis of the expected error, $E(\epsilon)$, as defined in the following relationship:

$$E(\epsilon) = B_f + B_p + B_a$$

where: B_f is the bias from field sampling,
B_p is the bias from sample preparation, and
B_a is the bias from sample analysis.

If suitable values for the reference samples are known, then the expected error is calculated as:

$$E(\epsilon) = \mu - E(Y)$$

where: μ is the reference value, and
$E(Y)$ is the expectation of the observed values.

In this study, a standard soil reference material consisted of natural non-synthetic soil, making it difficult to establish a single reference value. Instead, a range of acceptable values defined by confidence intervals from previous characterizations is used in lieu of the reference value. All observed values within that range are assumed to be equally reliable and, therefore, have zero bias. Accordingly, the error term can be described as:

$$\epsilon = \begin{cases} Y - U & \text{if } Y > U \\ 0 & \text{if } L \leq Y \leq U \\ Y - L & \text{if } Y < L \end{cases}$$

where: U is the upper reference value, and
L is the lower reference value.

So,

$$E(\epsilon) = \int_{Y>U} (Y - U)\, f(Y)\, dY + \int_{Y<L} (Y - L)\, f(Y)\, dY\ , \text{ and}$$

$$\hat{E}(\epsilon) = 1/n\ \left[\ \Sigma_{Y>U} (Y - U) + \Sigma_{Y<L} (Y - L)\ \right],$$

where: $\hat{E}(\epsilon)$ is the estimated expected error, and
n is the number of observed values.

Like imprecision, bias can vary with changes in concentration. In order to address this issue, reference materials at different concentrations are required. The homogeneity of the expected error across the range of concentration indicates the constancy of bias. If the bias is found to be constant across the range of concentration, no special correction is needed to normalize the error term. If the bias is found to vary with concentration, then the step function technique described in the imprecision section is used to pool the biases from different concentrations.

In the Mid-Appalachian survey, nearly equal quantities of standardized reference samples were allocated to each sampling crew (field audit samples) and analytical laboratory (laboratory audit samples). System-wide bias can be evaluated using the field audit samples. Throughout the data acquisition process, it is assumed that the primary sources of bias are derived from procedural or instrumental differences among the analytical laboratories. Inaccuracy stemming from instrument calibration, sample contamination, etc., can cause laboratory measurements to be biased high or low in relation to a reference value. If the laboratory bias is constant across different analyte concentrations for the population of laboratories, then a single audit sample concentration is sufficient to control and estimate the analytical bias.

For this study, it is assumed that bias does not change on the set Ω from which the routine samples take values. However, if bias differs significantly between analytical laboratories, then it can be considered to be a random variable which takes different values for different laboratories. The expected error in that case is:

$$E(\epsilon) = E\{E_L(\epsilon)\}$$

where: $E_L(\epsilon)$ is the expected error for laboratory L.

Therefore,

$$E_i(\epsilon) = E_L(\epsilon) = B_L \text{ for laboratory L,}$$

and:

$$E[E_L(\epsilon)] = \Sigma B_L P_L .$$

Accordingly, bias can be estimated using the reference sample data from each analytical laboratory. The relative frequency of the routine samples analyzed by each laboratory can be used to estimate probabilities.

Laboratory Differences

It is possible that laboratory inaccuracy may differ significantly from one laboratory to another. In this event, laboratories can be evaluated for the significance of these differences. The estimates of conditional error expectations can be used to test the significance of the analytical bias. In the Mid-Appalachian survey, the homogeneity of conditional error expectations among laboratories were studied by using appropriate *t* tests or *F* tests. The interlaboratory differences comparison is a laboratory evaluation aspect and not a data evaluation aspect, hence, no error component criteria can be derived for the data uncertainty estimates.

Laboratory Trends

It is possible that inaccuracy is caused by contamination effects, instrumental drift, or some other systematic or irregular effect over time. For each laboratory, these effects can be determined by examining temporal intralaboratory trends. Standard regression techniques applied to the laboratory reference sample data were used to identify any temporal patterns in the observed analytical laboratory uncertainty.

Estimation of Overall Measurement Uncertainty

The overall measurement uncertainty is calculated as a δ^2 term defined for the expected squared error using the summation of the appropriate imprecision and bias terms. The expected variance is a function of within-batch and between-batch imprecision and the expected error is a function of bias across laboratories. The expected squared error can be described as follows:

$$\begin{aligned}\delta^2 = E(\epsilon^2) &= E\{E_i(\epsilon^2)\} \\ &= E\,[E_i\{\epsilon - E_i(\epsilon)\}^2 + E^2{}_i(\epsilon)] \\ &= E(\sigma_i^2) + E\{E_i^2(\epsilon)\} \\ &= E\{V_W(\epsilon) + V_B(\epsilon)\} + E\{E^2{}_L(\epsilon)\}\end{aligned}$$

Accordingly, the appropriate operator is placed on the squared error terms within each interval, which allows the overall measurement uncertainty to be expressed in the reporting units of the variable of interest, as follows:

$$\begin{aligned}\delta &= E \surd\ \sigma_i^2 + E_i^2(\epsilon) \\ &= E \surd\ V_W(\epsilon) + V_B(\epsilon) + E^2(\epsilon)\end{aligned}$$

The estimate of measurement imprecision is the pooled value of the error mean sum of squares across different concentration ranges. In some surveys, it may not be possible to estimate inaccuracy due to bias and, consequently, the total error mean sum of squares. In this event, the error variance can be pooled knowing that the result provides a measure of uncertainty due to measurement imprecision only.

Results and Discussion

Quality assurance data from the DDRP Mid-Appalachian soil survey were used to estimate the overall measurement uncertainty associated with the soil chemistry data. The modified hierarchical design implemented in the survey allowed the individual components of overall measurement uncertainty for the entire range of analyte concentration to be estimated. One exception to this is the analytical imprecision estimate, which was based on data from three types of laboratory audit samples encompassing the low- and median-ranges of concentration only. This estimate, however, was deemed more reliable than the estimate calculated from duplicate samples provided by the laboratories.

The measurement uncertainty was defined as the expected squared error as previously described and was derived by estimating $\sigma^2{}_W$, $\sigma^2{}_B$, and $E^2(\epsilon)$ across specific partitioned intervals of analyte concentration. The duplicate/routine sample and laboratory audit sample data sets were used to estimate imprecision, and the laboratory audit sample data sets were used to estimate bias.

As previously described, three separate data collection stages were evaluated for their respective data measurement uncertainties. These are expressed as δ_1, δ_2, and δ_3 values which represent the analytical uncertainty, the confounded sample preparation and analytical uncertainty, and the confounded field sampling, sample preparation, and analytical uncertainty, respectively. In order to obtain uncertainty estimates for the routine sample population as defined by soil sampling class/horizon configurations, the standard deviations from all possible configurations were pooled for a given soil characteristic. This pooled uncertainty estimate, δ_4, generally shows a marked increase relative to the confounded three-stage measurement uncertainty estimated as δ_3. A relative comparison of δ_3 and δ_4 can be used as one possible approach for estimating the magnitude of measurement error in relation to the overall variability in the routine sample population.

As expected, the overall uncertainty increased with increasing sources of confounded uncertainty such that $\delta_2 < \delta_3 < \delta_4$. For some parameters, however, $\delta_1 > \delta_2$. In these situations, a lack of laboratory audit sample data in some of the intervals made it impossible to construct a reliable estimate of the uncertainty across the intervals. The δ_1 estimates are considered to be conditional on those intervals for which uncertainty estimates are available.

Table 2 provides two different examples of the overall measurement uncertainty estimates, δ_3, for the concentration intervals within which the measurement uncertainty is considered to be constant. For each interval, estimates of within-batch imprecision, between-batch imprecision, bias, expected squared error, and the empirical estimates of the proportion of routine samples in each interval are provided. It was expedient to pool the error characteristics for the different

Table 2. Selected overall measurement uncertainty estimates for different intervals

Parameter	Interval	σ_W	σ_B	$E(\epsilon)$	$\sqrt{E(\epsilon^2)}$	P(F)	
Extr. sulfate	< 7.0	0.588	0.644	0.022	0.872	0.145	
(mg S/kg)	7.0-15.0	1.707	1.430	0.022	2.227	0.481	$\delta_3 = 1.913$
	15.0-18.0	2.508	0.036	0.022	2.508	0.190	
	> 18.0	0.632	1.135	0.022	1.299	0.184	
Exch. calcium	< 0.2	0.039	0.028	0.002	0.048	0.204	
(meq/100g)	0.2-1.0	0.070	0.023	0.002	0.074	0.505	$\delta_3 = 0.296$*
	1.0-5.0	0.862	.	0.002	0.862*	0.281	
	> 5.0	0.655	.	0.002	0.655*	0.011	

σ_W is the within-batch imprecision for interval

σ_B is the between-batch imprecision for interval

$E(\epsilon)$ is the bias for interval

$\sqrt{E(\epsilon^2)}$ is the measurement uncertainty for interval

P(F) is the empirical proportion of routine samples in interval

δ_3 is the overall measurement uncertainty across intervals, calculated from field duplicate samples

* is a partial estimate (underestimate) due to incomplete data in one or more intervals

concentration intervals, hence, the corresponding summary δ value pooled across the intervals is also given for the two parameters of interest.

It is evident that the data for extractable sulfate generally have high precision across the range of concentration, in relation to the survey objective of 30 percent precision for the field duplicate samples. The estimated overall measurement uncertainty for sulfate is approximately 1.91 milligrams sulfur per kilogram of soil (mg S/kg), which is small in relation to the mean sulfate concentration of 17.24 mg S/kg. The estimated overall measurement uncertainty for exchangeable calcium is approximately 0.30 milliequivalents per 100 grams of soil (meq/100g), which is large in relation to the mean calcium concentration of 0.93 meq/100g. This relatively large uncertainty can be attributed to the generally low concentrations of exchangeable calcium in the population of soil samples collected.

Table 3 provides a summary of data uncertainty estimates for the various stages of measurement and the sample population. In nearly all cases, $\delta_4 > \delta_3 > \delta_2$, while δ_1 and δ_2 are irregular in their magnitude. Commonly, the δ_1 value is relatively high because it is a conditional estimate based on incomplete sample data. To compare the data uncertainties of any two data sets, a data user may wish to relate the data uncertainty measures with the population mean of the routine samples which is provided for reference in the table. A comparison of δ_3 and δ_4 values can be used as a basic estimate of the relative effect of measurement uncertainty on the overall uncertainty of the routine data.

Table 3. Uncertainty estimates associated with the Mid-Appalachian survey.

Parameter	Reporting units	Data uncertainty estimate[a]				Mean[b]
		δ_1	δ_2	δ_3	δ_4	
Soil pH	pH units	0.078	0.087	0.114	0.473	4.751
Exch. calcium	meq/100g	0.032**	0.055*	0.296*	1.091*	0.930
Exch. magnesium	meq/100g	0.017**	0.019*	0.026*	0.446*	0.418
Exch. potassium	meq/100g	0.007**	0.011*	0.009*	0.094*	0.133
Exch. sodium	meq/100g	0.004**	0.005*	0.006*	0.014*	0.016
Exch. capacity	meq/100g	1.407	1.661	1.633	4.667	7.242
Exch. acidity	meq/100g	1.660*	1.652	1.832	5.582	11.197
Extr. iron	weight %	0.025*	0.030	0.035	0.305	0.347
Extr. aluminum	weight %	0.025**	0.022**	0.027**	0.165*	0.190
Extr. sulfate	mg S/kg	1.626*	1.623	1.913	27.175	17.244
Total carbon	weight %	0.070**	0.059**	0.185*	1.213*	1.438

[a] δ_1 = imprecision due to analytical error; computed from laboratory audit samples

δ_2 = imprecision due to preparation and analytical error; computed from preparation duplicates

δ_3 = imprecision due to field sampling, preparation, and analytical error; computed from field duplicates

δ_4 = imprecision due to measurement sources and sample population uncertainty; computed from routine samples grouped in sampling class/horizon configurations

[b] mean concentration of the soil samples in the survey

* partial estimate (underestimate) due to incomplete data for one or more intervals

** conditional estimate (overestimate) due to lack of data in one or more intervals

Summary and Conclusions

The objective of the modified hierarchical design was to control and estimate measurement precision and accuracy during the Mid-Appalachian survey. These estimates are very useful in assessing the quality of environmental data. When the soil characteristics of a survey region are expected to be wide ranging, it is likely that the measurement imprecision will vary for different intervals across the range of concentration for most variables. In this event, measurement uncertainty can be estimated separately for each of the intervals, and the overall measurement uncertainty can be estimated by a step function which pools the different intervals. The relative effect of measurement uncertainty on the overall data uncertainty in the routine samples can be assessed using the weighted average of the step function with respect to the routine samples. The data from the Mid-Appalachian survey suggest that data uncertainty, with respect to imprecision, increases with increasing confounded sources of uncertainty.

In any survey design, measurement uncertainty should be controlled at an acceptable level. Unless there is evidence from previous data to reject the hypothesis that the measurement bias is constant for different intervals of analyte concentration, one source of reference soil material in a single concentration interval for each variable is sufficient to control and estimate measurement bias.

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Appendix K

Data Tracking and Verification Forms

This appendix contains some of the data tracking and verification forms used by the QA staff to document batch sample data checks performed by the analytical laboratories during the MASS sample analysis. Included are examples of the DDRP Form 102 (shipping form), DDRP Form 500 (batch confirmation/reanalysis form, and DDRP Forms 600A and 600B (internal consistency confirmation forms).

DIRECT/DELAYED RESPONSE PROJECT (DDRP)
SHIPPING FORM 102

DATE RECEIVED
BY DATA MGT. __ __ __ __ __ __ __
D D M M M Y Y

D D M M M Y Y

Prep Lab ID ______________________ Date Received __ __ __ __ __ __ __

Batch ID ______________________ Date Shipped __ __ __ __ __ __ __

Analytical Lab ID ______________________

SAMPLE NO.	BULK SAMPLES		PH < 8.5	RETURNED TO LEMSCO (CHECK Y IF YES)
	SHIPPED	RECEIVED		
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
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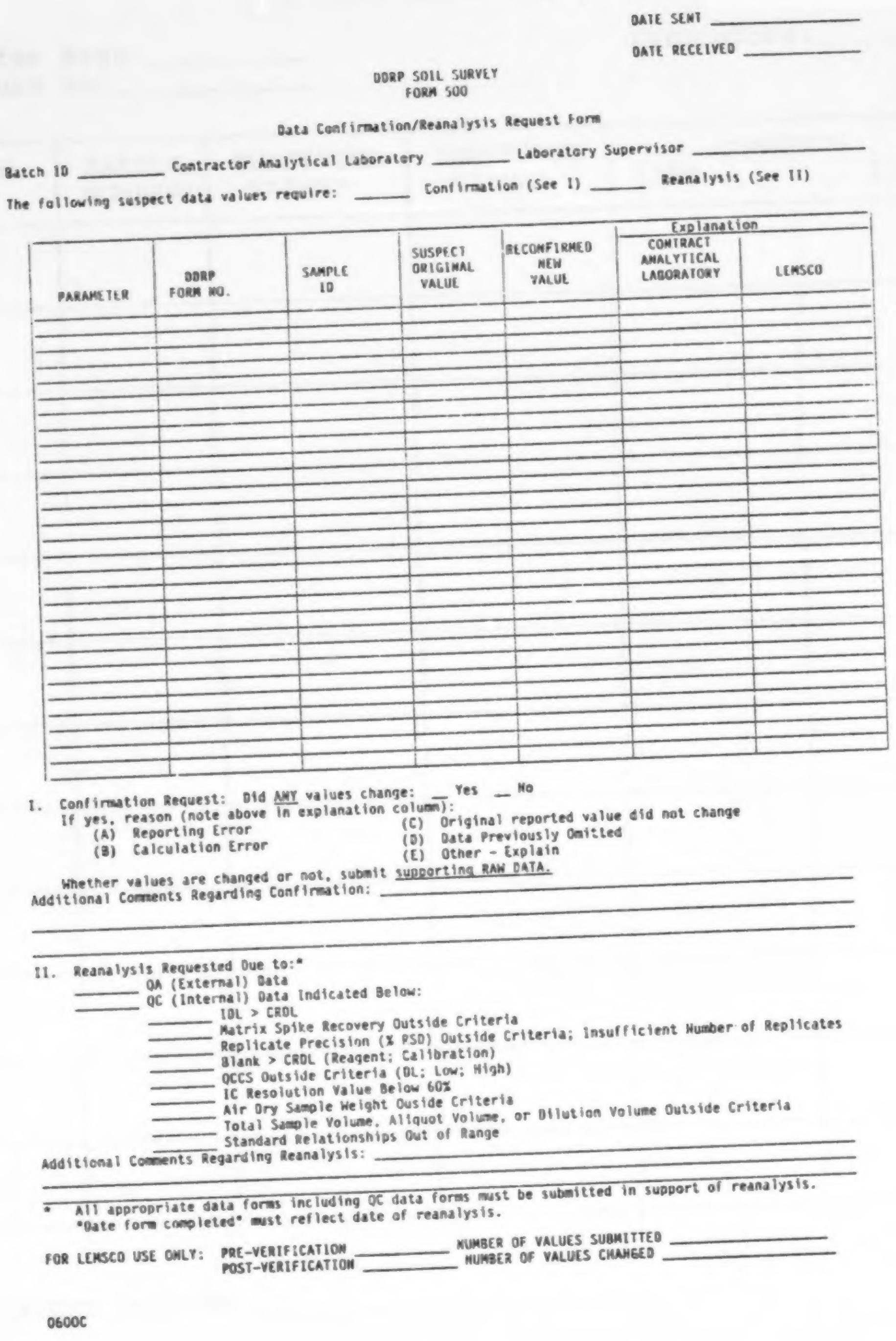
40				

Signature of Preparation Laboratory Manager: ______________________

Comments:

Figure K-1. DDRP Form 102 (shipping form).



DATE SENT ____________

DATE RECEIVED ____________

DDRP SOIL SURVEY
FORM 500

Data Confirmation/Reanalysis Request Form

Batch ID ________ Contractor Analytical Laboratory ________ Laboratory Supervisor ____________

The following suspect data values require: ______ Confirmation (See I) ______ Reanalysis (See II)

PARAMETER	DDRP FORM NO.	SAMPLE ID	SUSPECT ORIGINAL VALUE	RECONFIRMED NEW VALUE	Explanation	
					CONTRACT ANALYTICAL LABORATORY	LEMSCO

I. Confirmation Request: Did ANY values change: __ Yes __ No
If yes, reason (note above in explanation column):
(A) Reporting Error
(B) Calculation Error
(C) Original reported value did not change
(D) Data Previously Omitted
(E) Other - Explain

Whether values are changed or not, submit supporting RAW DATA.

Additional Comments Regarding Confirmation: ____________________

II. Reanalysis Requested Due to:*
- ______ QA (External) Data
- ______ QC (Internal) Data Indicated Below:
  - ______ IDL > CRDL
  - ______ Matrix Spike Recovery Outside Criteria
  - ______ Replicate Precision (% RSD) Outside Criteria; Insufficient Number of Replicates
  - ______ Blank > CRDL (Reagent; Calibration)
  - ______ QCCS Outside Criteria (DL; Low; High)
  - ______ IC Resolution Value Below 60%
  - ______ Air Dry Sample Weight Ouside Criteria
  - ______ Total Sample Volume, Aliquot Volume, or Dilution Volume Outside Criteria
  - ______ Standard Relationships Out of Range

Additional Comments Regarding Reanalysis: ____________________

* All appropriate data forms including QC data forms must be submitted in support of reanalysis. "Date form completed" must reflect date of reanalysis.

FOR LEMSCO USE ONLY:
PRE-VERIFICATION ________ NUMBER OF VALUES SUBMITTED ____________
POST-VERIFICATION ________ NUMBER OF VALUES CHANGED ____________

0600C

Figure K-2. DDRP Form 500 (data confirmation/reanalysis request form).

DDRP FORM 600A

Parameter Name:__________ Laboratory:__________
DDRP Form No:____________

BATCH	SAMPLE NUMBER	SUSPECTED VALUES	CORRECTED VALUES	COMMENTS LABS	 LESC

LABORATORY MANAGER ___________________________

Figure K-3. DDRP Form 600A (internal consistency confirmation form).

DDRP FORM 600B

Parameter Name:__________

DDRP Form No:____________

Laboratory:__________

BATCH	SAMPLE NUMBER	SUSPECTED VALUES	CORRECTED VALUES	COMMENTS LABS	 LESC

LABORATORY MANAGER ____________________________

Figure K-4. DDRP Form 600B (internal consistency confirmation form).